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Synthesis, Structure, and Thermal Stability of a New 2D Copper(II) Coordination Polymer Based on 2-Propyl-1*H*-Imidazole-4,5-Dicarboxylate[1]

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Abstract—A new Cu(II) coordination polymer with singly deprotonated 2-propyl-imidazole-4,5-dicarboxylate (H_3PIDC) as bridging ligand of formula $[Cu(H_2PIDC)_2]_n$ (**I**) was synthesized and characterized by IR, element analysis, and X-ray diffraction method. Compound **I** crystallizes in the monoclinic space group $P2_1/n$ with cell parameters $a = 8.332(1)$, $b = 10.160(1)$, $c = 11.228(1)$ Å, $\beta = 91.13(1)°$, $V = 950.3(2)$ Å^3, $M_r = 457.88$, $Z = 2$, $\rho_c = 1.600$ g/cm^3, $F(000) = 470$, $\mu = 1.202$ mm^{-1}, $R_1 = 0.0412$, and $wR_2 = 0.1064$ for 2015 observed reflections. The Cu^{2+} ions are coordinated by four H_2PIDC^- ligands via N,O-chelating and O-bridging mode to form 2D layer planes, which are further linked by intermolecular hydrogen bonds and weak interactions into a 3D framework.

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INTRODUCTION

In the past two decades, increased interests have been devoted to the rational design and synthesis of coordination polymers because of their unusual topologies [1–3] and potential applications as functional materials in fields, such as magnetism [4–6], catalysts [7], and luminescent materials [8–10]. Multifunctional organic ligands and transition metal ions play an important role in constructing the extended structure of the coordination polymers [11–13], so the deliberate selection of metals and multifunctional ligands to prepare interesting polymeric frameworks is one of the most attractive topics [14–16]. It is known that Cu^{2+} ions are able to be coordinated simultaneously in solution by both oxygen-containing and nitrogen-containing ligands. Imidazole dicarboxylate ligands have attracted much attention in preparation of coordination polymers due to their various bridging conformations, which derives from both imidazole and carboxylate functionalities [15–17]. In addition, this ligand can be successively deprotonated to generate H_2IDC^-, $HIDC^{2-}$, and IDC^{3-} at different pH values, which has resulted in a large diversity of coordination polymers [18–21]. Recently, the propyl derivative of H_3IDC, 2-propyl-1*H*-imidazole-4,5-dicarboxylate (H_3PIDC), has been applied to constructing coordination polymers [22–25]. However, the Cu(II) polymer containing the H_3PIDC ligand is not prepared; much work is still necessary to be done to understand the coordination chemistry of H_3IDC. Herein, we obtain a 2D coordination polymer $[Cu(H_2PIDC)_n]$ (**I**) by reacting of H_3PIDC with $Cu(Ac)_2 \cdot H_2O$. This paper describes its synthesis, structure and thermal stability.

EXPERIMENTAL

All the chemicals were obtained from commercial sources. Elemental analyses were performed on a PerkinElmer 240 elemental analyzer. The infrared spectrum was recorded in KBr pellet in the range of 4000–600 cm^{-1} on a Nicolet Avatar-360 spectrometer. The TG curve was obtained with an Exstar 6000 analyzer in nitrogen at a heating rate of 10°C/min from 30 to 800°C.

Synthesis of I. A mixture of $Cu(Ac)_2 \cdot H_2O$ (0.0002 mol, 0.040 g), H_3PIDC (0.0002 mol, 0.040 g) and water (6.0 mL) sealed in a 25 mL Teflon-lined stainless steel vessel was heated to 130°C at a rate of 20°C/h, and held at this temperature for 72 h, then cooled to room temperature within 20 h. Pink block crystals of **I** were isolated in 75% yield after being washed with distilled water and dried in air. IR (ν, cm^{-1}): 3456 ν_{as}(N–H), 1716 $\nu_{as}(COO^-)$, 1532 $\nu_s(COO^-)$, 1562 ν_s(C=N).

For $C_{16}H_{18}N_4O_8Cu$

anal. calcd., %:	C, 41.64;	H, 3.96;	N, 12.24.
Found, %:	C, 41.76;	H, 3.89;	N, 12.06.

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[1] The article is published in the original.

Table 1. Crystallographic and experimental data for compound **I**

Parameter	Value
Crystal shape; color	Block; blue
Crystal size, mm	0.20 × 0.21 × 0.26
Crystal system	Monoclinic
Space group	$P2_1/n$
a, Å	8.332(1)
b, Å	10.160(1)
c, Å	11.228(1)
β, deg	91.13(1)
V, Å^3	950.3(2)
Z	2
μ_{Mo}, mm^{-1}	1.202
θ Range, deg	2.70–28.22
Limiting indices h, k, l	$-10 \le h \le 11$, $-13 \le k \le 13$, $-14 \le l \le 14$
Measured reflections	8539
Independent reflections	2027
Observed reflections, $I > \sigma(I)$	2015
T_{min} and T_{max}	0.7747 and 0.8292
F(000)	470
Goodness of fit on F^2	1.052
R_1, wR_2 ($I > 2\sigma(I)$)	0.0412, 0.1064
R_1, wR_2 (all data)	0.0480, 0.1120
$\Delta\rho_{max}$ and $\Delta\rho_{min}$, e Å^{-3}	0.947 and –1.120

Note: $w = 1/[\sigma^2(F_o^2) + (0.1147P)^2 + 24.4872P]$, $P = (F_o^2 + 2F_c^2)/3$.

X-ray structure determination. A single crystal of compound **I** (0.20 × 0.21 × 0.26 mm) was put on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromatic MoK_α radiation ($\lambda = 0.71073$ Å) at 296(2) K using φ/ω scan technique. The structure was solved by direct methods with SHELXS-97 [26]. Crystal data collection, parameters, and refinement statistic for compound **I** are listed in Table 1. Refinement on F^2 was performed using SHELXL-97 [27] by a full-matrix least-squares method with anisotropic parameters for all non-hydrogen atoms. All hydrogen atoms were assigned with common isotropic displacement factors refined with restraints. Selected bond distances and bond angles for compound **I** are listed in Table 2. The hydrogen bonds are given in Table 3.

Supplementary material for structure **I** has been deposited with the Cambridge Crystallographic Data Centre (no. 812384; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Asymmetric unit of compound **I** consists of one Cu(II) atom and two singly deprotonated H_2PIDC^- groups which display strong intramolecular hydrogen bonds O(2)–H(3)···O(4) (O···O 2.556(3) Å) and angle 174.0°. The four carboxylic oxygen atoms of H_2PIDC^- are not in the plane of the imidazole ring, with the deviations of –0.115, 0.097, 0.162, and 0.221 Å out of the plane for O(1), O(2), O(3), and O(4), respectively.

Table 2. Selected bond lengths (Å) and bond angles (deg) for compound **I**

Bond	d, Å	Bond	d, Å	Bond	d, Å
Cu(1)–N(1)	1.971(2)	Cu(1)–O(1*B*)	2.512(2)	O(3)–C(4)	1.259(3)
Cu(1)–N(1*A*)	1.971(2)	Cu(1)–O(1*C*)	2.512(2)	O(4)–C(4)	1.258(3)
Cu(1)–O(3)	2.005(2)	O(1)–C(5)	1.214(3)		
Cu(1)–O(3*A*)	2.005(2)	O(2)–C(5)	1.311(3)		
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
N(1)Cu(1)N(1*A*)	180.0(2)	O(1*B*)Cu(1)O(3*A*)	79.63(6)	N(1*A*)Cu(1)O(3)	96.87(7)
O(3)Cu(1)O(3)	180.0(1)	N(1*A*)Cu(1)O(3*A*)	83.13(7)	O(1*C*)Cu(1)O(3)	79.63(6)
O(1*B*)Cu(1)O(1*C*)	180.0(6)	O(1*C*)Cu(1)O(3*A*)	100.4(6)	O(1*C*)Cu(1)N(1)	89.47(7)
N(1)Cu(1)O(3*A*)	96.87(7)	O(1*B*)Cu(1)N(1*A*)	89.47(7)	O(1*B*)Cu(1)N(1)	90.53(7)
N(1)Cu(1)O(3)	83.13(7)	O(1*C*)Cu(1)N(1*A*)	90.53(7)	O(1*B*)Cu(1)O(3)	100.4(6)

Note: Symmetry codes: (*A*) $-x$, $-y$, $-z$; (*B*) $x + 0.5$, $-y + 0.5$, $z - 0.5$; (*C*) $-x - 0.5$, $y - 0.5$, $-z + 0.5$.

The perspective view of the compound with atomic labeling scheme is shown in Fig. 1.

In the structure of **I**, Cu(II) atom shows a slightly distorted octahedral environment, coordinated by four H_2PIDC^- groups. The equatorial plane is composed of two carboxylate oxygen atoms (O(3) and O(3*A*)) and two imidazole nitrogen atoms (N(1) and N(1*A*)) from two H_2PIDC^- ions in an N–O bidentate coordination mode. The axial positions are occupied by oxygen atoms (O(1*B*) and O(1*C*)), belonging to the carboxylate groups of the other two H_2PIDC^- ligands. The Cu–N bond distances (1.971(2) Å, Table 1) and Cu–O bond distance (2.005(2) Å, Table 1) in the equatorial positions are close to those reported values for the Cu(II) complexes containing dicarboxylate ligands [28–30]. The long Cu–O bond distances (2.512(2) Å) in the axial positions indicate a weak coordination interaction and is attributed to the effect of Jahn–Teller elongation [31, 32]. The angles of N(1)Cu(1)O(3) and O(1*B*)Cu(1)O(3*A*) are 83.13(7)° and 79.63(6)°, respectively. These angles indicate the slightly distorted octahedral structure of the Cu(II) complex. Four H_2PIDC^- groups act as μ_3-bridges and link four Cu^{2+} ions into a molecular square of $[Cu_4(\mu_3\text{-}H_2PIDC)_4]$, which resides on the inversion center and the four metal ions are exactly coplanar. The Cu···Cu separations of the Cu_4 square are 8.695(7) Å, and the vertex angles are 71.50(1)° and 108.5(1)° (Fig. 2). These Cu_4 squares then extend in different directions to form a 2D layer structure (Fig. 3), which are further connected by intermolecular hydrogen bonds (N(2)–H(2)···O(4)$^\#$ (N···O 2.834(3) Å, angle NHO 167°; $^\#0.5 + x, 0.5 - y, 0.5 + z$) between imidazole nitrogen atoms and carboxylate oxygen atoms on the adjacent layers into a 3D framework (Fig. 4). Weak intermolecular interactions C(6)–H(6*A*)···O(2) (C···O 3.449(2) Å, angle CHO 132°; C(7)–H(7*B*)···O(2) (C···O 3.362(3) Å, angle CHO 139°) also play an important role in constructing the 3D network.

Table 3. Hydrogen bond geometry for compound **I***

Contect D–H···A	Distances, Å			Angle DHA, deg
	D–H	H···A	D···A	
N(2)–H(2)···O(4*D*)	0.86	1.99	2.834(3)	167.0
O(2)–H(3)···O(4)	0.82	1.74	2.556(3)	174.0

* Symmetry code: (*D*) $0.5 + x, 0.5 - y, 0.5 + z$.

In order to evaluate the thermal stability of complex **I**, TG experiment was carried out and the thermal curve was illustrated in Fig. 5. The figure shows a weight loss of 43.06% in the range of 234 to 352°C, which is attributed to release of one H_2PIDC^- ion (calcd.: 43.11%). Complex **I** continues to decompose

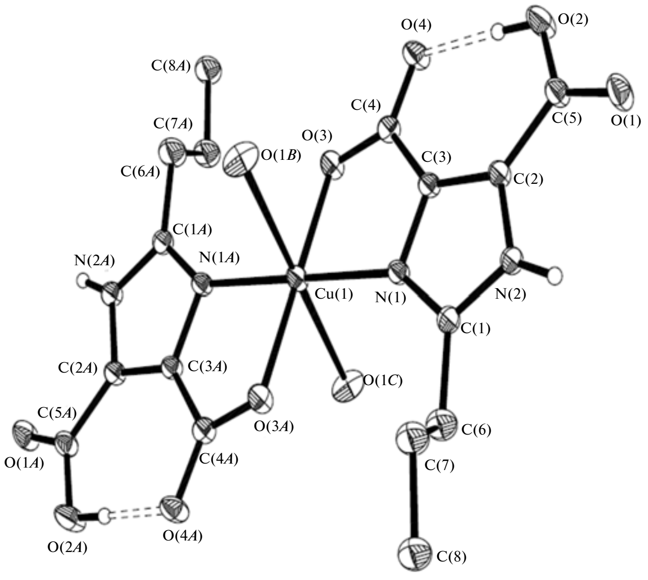

Fig. 1. Molecular structure of **I** at 30% ellipsoid. The hydrogen atoms of propyl groups are omitted for clarity. Symmetry codes: (*A*) $-x, -y, -z$; (*B*) $x + 0.5, -y + 0.5, z - 0.5$; (*C*) $-x - 0.5, y - 0.5, -z + 0.5$.

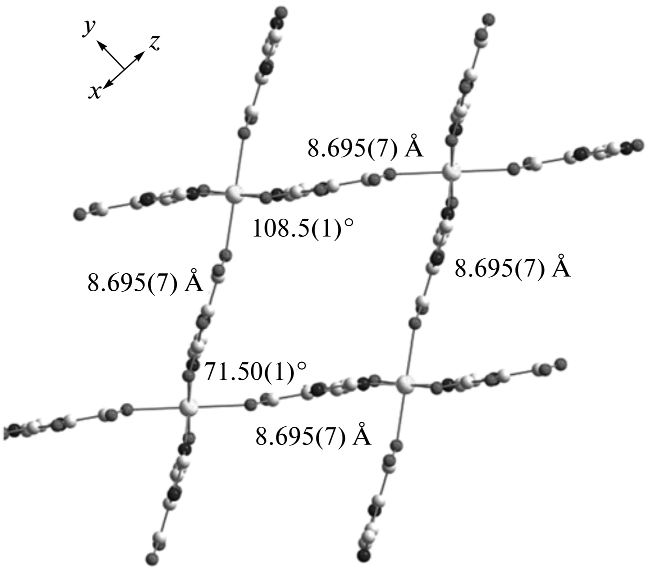

Fig. 2. View of the molecule square along the *z* direction. The propyl and hydrogen atoms are omitted for clarity. Symmetry codes: (*B*) $-x, y + 0.5, -z + 0.5$.

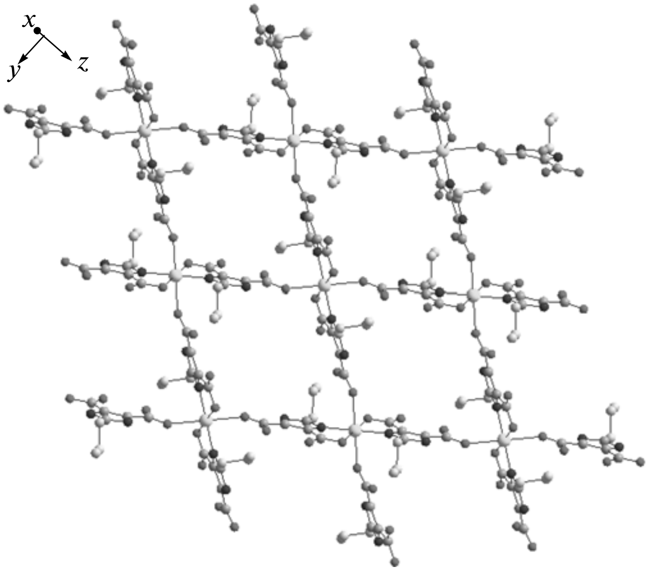

Fig. 3. View of the 2D layer structure along the *x* direction.

up to 485°C and the remainder is copper oxide, who account for 17.42% (calcd.: 17.37%). The stepwise decompositon procedure of the H_2PIDC^- ligands is consistent with the differences in coordination modes (N,O-chelating *vis* O-bridging) and bond distances of Cu(1)–O (2.005(2) *vis* 2.512(2) Å, Table 2). The experiment shows the thermal stability of complex **I** is good enough for various use in normal conditions.

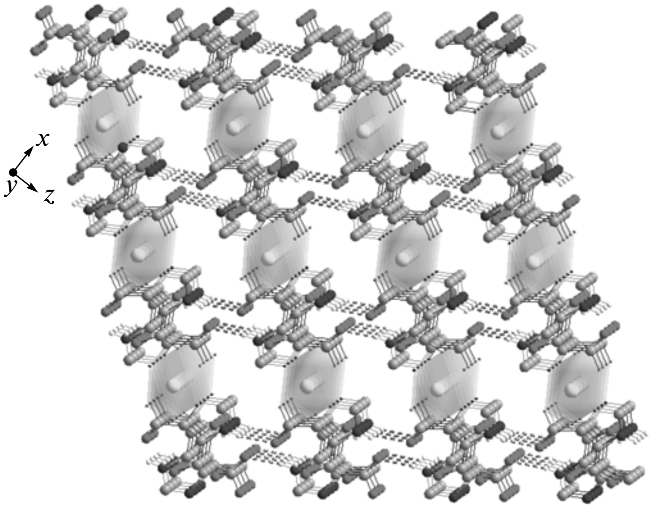

Fig. 4. View of the 3D network along the *y* direction. The propyl groups are omitted for clarity.

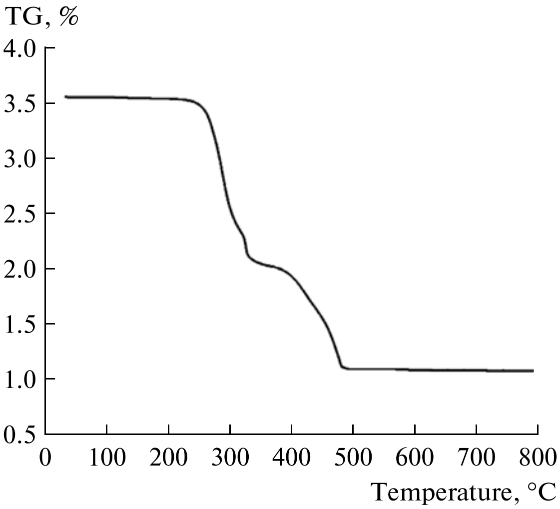

Fig. 5. TGA curve for complex **I**.

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