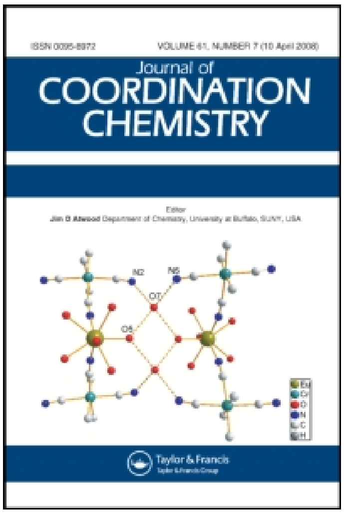

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The synthesis and structure of a novel 1D copper(II) weak coordination polymer with 2,6-pyridinedicarboxylic acid

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THE SYNTHESIS AND STRUCTURE OF A NOVEL 1D COPPER(II) WEAK COORDINATION POLYMER WITH 2,6-PYRIDINEDICARBOXYLIC ACID

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A novel copper complex, $[Cu(dipic)(H_2O)_2]_n$ ($H_2dipic = 2,6$-pyridinedicarboxylic acid), was synthesized and its crystal structure determined by X-ray diffraction. The complex has a polymeric structure of infinite one-dimensional (1D) zigzag chains, consisting of six-coordinate Cu(II) units. Each copper(II) ion is in a distorted octahedral environment with a $CuNO_5$ core: two oxygen atoms and one nitrogen atom from one dipic anion, one oxygen atom from an adjacent dipic ligand and two oxygen atoms from coordinated water. Each dipic anion connects two copper ions via a μ_2-oxygen atom. The zigzag 1D-chains are linked by extensive hydrogen bonds to form 2D infinite sheets.

Keywords: Crystal structure; Copper complex; 1D-chain; 2,6-Pyridinedicarboxylic acid

INTRODUCTION

Metal–organic coordination polymers with one-, two- or three-dimensional structures have attracted attention for their potential applications as photoelectric materials, catalysis carriers, sensors, etc. [1–6]. In the design and synthesis of polymeric complexes, various bridging and chelating ligands have been used extensively. Coordination bonds and hydrogen bonds are the major interactions in these assemblies. 2,6-Pyridinedicarboxylic acid (H_2dipic) is an efficient ligand with three coordinating sites. Polymeric structures of dipic complexes with transition and lanthanide metals have been reported, in which dipic not only chelates but also bridges to form diversified structures [7–13].

Several synthetic methods can be used to obtain new polymeric complexes [14–19]; hydrothermal synthesis has been demonstrated to be an effective and powerful technique for forming special coordination modes and high-dimensional structures [20]. In this work, we have designed and synthesized a new dipic complex with copper(II). Imidazole was introduced into the reaction system as a terminal ligand to reinforce

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the bridging ability of the dipic ligand. Although the imidazole did not participate in the complex structure, it may have some influence in forming the 1D zigzag chain. We report here the hydrothermal synthesis and crystal structure of the 1D polymeric complex $[Cu(dipic)(H_2O)_2]_n$.

EXPERIMENTAL

Reagent

Copper(II) perchlorate hexahydrate was prepared by literature methods [21]. Other chemical reagents were of analytical grade, obtained from commercial sources and used without further purification. (Caution! Perchlorate salts of transition metals and their complexes are potentially explosive; only a small amount should be prepared and handled with care.)

Synthesis

A mixture of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.4 mmol, 148 mg), H_2dipic (0.4 mmol, 66.9 mg), imidazole (0.8 mmol, 54.4 mg) and H_2O (18.0 mL) in the molar ratio 1 : 1 : 2 : 2500 was sealed in a 25-mL stainless steel reactor with a Teflon liner and heated to 140°C, kept at 140°C for 72 h, and then cooled slowly to 30°C at a rate of 2°C/h. Green plate crystals of the title complex were collected by filtration and washed with ethanol (2 × 5 mL). Yield 10%. Anal. Calcd. for $C_7H_7CuNO_6$(%): C, 31.70; H, 2.64; N, 5.82. Found: C, 31.44; H, 2.80; N, 5.69.

Physical Measurement

The IR spectrum of the complex in the range 400–4000 cm^{-1} was recorded in pellets with KBr using a Nicolet AVATAR 360 FT-IR spectrophotometer. The most salient feature of the IR spectrum of the compound is the existence of strong bands at 1650, 1620, 1580 attributed to ν(C=O) and 1354 cm^{-1} attributed to ν(C–O) stretching vibrations. A weak peak at 1605 cm^{-1} is assigned to the C=N group.

Structure Determination

Room-temperature (294 ± 1 K) single-crystal X-ray experiments were performed on a Bruker SMART 1000 CCD diffractometer equipped with graphite-monochromated Mo Kα radiation. Data collection and reduction were performed using SMART and SAINT software. An empirical absorption correction (SADABS) was applied to the raw intensities. The structures were solved by direct methods and refined by full-matrix least-squares based on F^2 using the SHELXTL program package. Nonhydrogen atoms were subjected to anisotropic refinement. The H-atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restraints. The crystal data and structure refinement parameters are listed in Table I.

TABLE I Crystal data and structure refinement for the title complex

Molecular formula	$Cu(C_7H_3NO_4)\cdot(H_2O)_2$
Molecular weight	264.68
Color and habit	Green plate
Crystal size (mm)	0.22 × 0.14 × 0.10
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	7.2223(19)
b (Å)	19.064(5)
c (Å)	6.4358(17)
α (°)	90.00
β (°)	107.110(4)
γ (°)	90.00
V (Å), Z	846.9(4), 4
Density (calcd.) (g/cm^3)	2.076
Reflections measured/unique	4764/1719
Absorption coefficient (mm^{-1})	2.588
λ (Å)	0.71073
$R1$	0.0248 (for observed data)
$wR2$	0.0597 (for observed data)
Goodness-of-fit	1.103

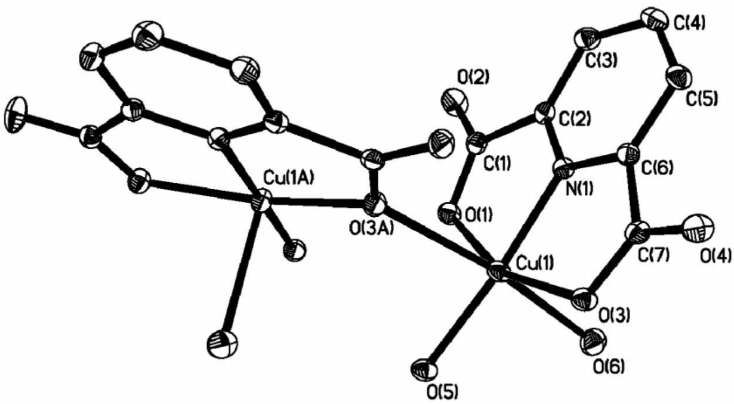

FIGURE 1 Molecular structure of the title complex showing 30% probability displacement ellipsoid.

RESULTS AND DISCUSSION

A perspective view of the title molecule with the atom numbering scheme is shown in Fig. 1. Selected bond lengths and angles are listed in Table II. In this complex, each copper(II) ion is six-coordinate in a distorted octahedral environment with a $CuNO_5$ core: two oxygen atoms [O(1), O(3)] and one nitrogen atom [N(1)] from one dipic anion, one oxygen atom [O(3A)] from an adjacent dipic ligand and two oxygen atoms [O(5), O(6)] from coordinated water molecules. The copper atom with two oxygen atoms and one nitrogen atom from one dipic anion and one water oxygen atom [O(5)] are approximately in a plane. The apical sites are occupied by one oxygen atom [O(3A)] from an adjacent dipic and one water oxygen atom [O(6)], which weakly coordinated [Cu(1)–O(6) = 2.4062(17) Å, Cu(1)–O(3A) = 2.4337(15) Å], as in previous reports [22]. Distorted stereochemistry is to be expected for Cu(II) as

TABLE II Selected bond lengths (Å) and bond angles (°) for the title complex

Cu(1)–N(1)	1.8979(18)	Cu(1)–O(5)	1.9431(15)
Cu(1)–O(1)	2.0440(16)	Cu(1)–O(3)	2.0593(15)
Cu(1)–O(6)	2.4062(17)	Cu(1)–O(3A)	2.4337(15)
O(1)–C(1)	1.281(3)	O(2)–C(1)	1.223(3)
O(3)–C(7)	1.280(3)	O(3)–Cu(1A)	2.4337(15)
O(4)–C(7)	1.235(3)	C(1)–C(2)	1.515(3)
C(6)–C(7)	1.521(3)		
N(1)–Cu(1)–O(5)	174.75(7)	N(1)–Cu(1)–O(1)	80.38(7)
O(5)–Cu(1)–O(1)	95.61(6)	N(1)–Cu(1)–O(3)	80.28(7)
O(5)–Cu(1)–O(3)	103.83(6)	O(1)–Cu(1)–O(3)	160.54(6)
N(1)–Cu(1)–O(6)	95.04(7)	O(5)–Cu(1)–O(6)	88.30(6)
O(1)–Cu(1)–O(6)	89.81(6)	O(3)–Cu(1)–O(6)	89.73(6)
N(1)–Cu(1)–O(3A)	92.02(6)	O(5)–Cu(1)–O(3A)	84.13(6)
O(1)–Cu(1)–O(3A)	83.61(6)	O(3)–Cu(1)–O(3A)	99.23(5)
O(6)–Cu(1)–O(3A)	169.42(6)	C(1)–O(1)–Cu(1)	114.52(13)
C(7)–O(3)–Cu(1)	113.91(13)	C(7)–O(3)–Cu(1A)	127.15(13)
Cu(1)–O(3)–Cu(1A)	118.70(7)		

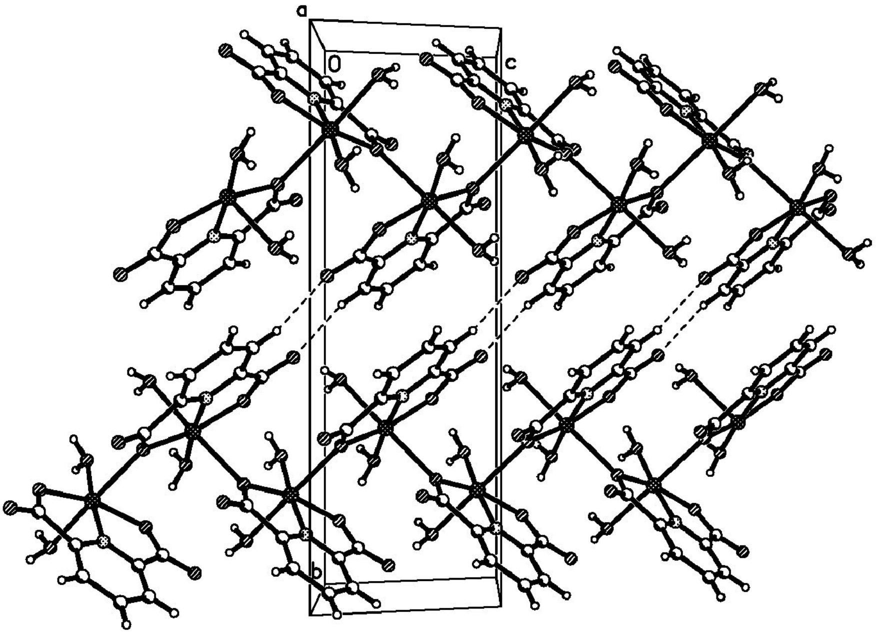

FIGURE 2 Packing view along the *a* direction of the polymer $[Cu(dipic)(H_2O)_2]_n$ with interchain hydrogen bonds.

a consequence of the nonspherical symmetry of the d^9 electronic configuration. This is usually ascribed to the Jahn–Teller effect with associated vibronic coupling [23,24]. Each dipic anion connects two copper ions: one as a three-chelating ligand [O(1), O(3), N(1)] and another via a μ_2-oxygen atom [O(3)]. Oxygen atoms O(2) and O(4) are not coordinated. In this case, the C–O distances [O(2)–C(1) = 1.223(3)Å, O(4)–C(7) = 1.235(3)Å, O(1)–C(1) = 1.281(3)Å, O(3)–C(7) = 1.280(3)Å] are generally shorter than other C–O distances, indicating the conjugation of the double bond after deprotonation.

The structure consists of one-dimensional (1D) zigzag chains running parallel to the *c* axis. Two adjacent copper atoms are linked via a μ_2-oxygen atom with a Cu–Cu distance of 3.870 Å. Extensive hydrogen bonds are formed between the oxygen atoms of the coordinated waters in one chain and the uncoordinated carboxylic oxygen atoms in the adjacent chain to form two-dimensional planes ($d_{O\cdots O} = 2.727$ Å, $d_{O\cdots H} = 1.886$ Å, $\angle OHO = 170.04°$). The packing view of the two-dimensional planes built by interchain hydrogen bonds of the polymer is shown in Fig. 2.

CONCLUSION

The influence of imidazole on the topological structures of polymers lies in controlling the acidity. Coordination polymers of transition metals and rare-earth metals with 2,6-pyridinedicarboxylic acid that consist of high-dimensional structures or mono-, multinuclear structures have been reported [7–13]. The zigzag 1D-chains of the title compound are markedly different, perhaps because the imidazole deprotonates 2,6-pyridinedicarboxylic acid ($pK_a = 6.95$) and prevents formation of the mononuclear 1 : 2 complex of the copper with the acid. The formation of the title complex may be due to different reaction conditions, but detailed understanding is lacking.

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Supplementary Data

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 227575. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk) or may be obtained from the corresponding author Xiaoqing Wang.

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