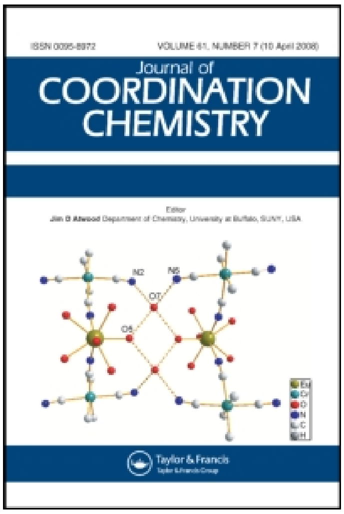

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Novel hydrogen-bonded three-dimensional network complexes containing copper-pyridine-2,6-dicarboxylic acid

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NOVEL HYDROGEN-BONDED THREE-DIMENSIONAL NETWORK COMPLEXES CONTAINING COPPER-PYRIDINE-2,6-DICARBOXYLIC ACID

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The novel complex $(H_3O)_2[Cu(2,6\text{-pydc})_2]\cdot H_2O$ (pydc = pyridinedicarboxylic acid) (**1**) has been synthesized in aqueous solution and characterized by single-crystal X-ray diffraction, elemental analyses and IR spectra. X-ray structural analysis revealed that the novel complex possesses both π–π stacking and hydrogen-bonding interactions for three-dimensional (3D) networks. Crystal data for **1**: $a = 13.454(3)$, $b = 10.266(2)$, $c = 13.783(3)$ Å, $\alpha = 90.00$, $\beta = 115.29(3)$, $\gamma = 90.00°$, $Z = 3$, $R_1 = 0.0423$, $wR_2 = 0.1217$.

Keywords: π–π stacking; Hydrogen-bonding interactions; Three-dimensional (3D) networks; 2,6-Pyridinedicarboxylic acid

INTRODUCTION

In recent years, crystal engineering of supramolecular architectures based on metal and organic building blocks has emerged as an exciting area of supramolecular chemistry because of its novel and diverse topologies and potential applications in host–guest chemistry, catalysis, electrical conductivity and magnetism [1,2]. The connection of metal-organic coordination networks based on complexes of transition metals and multifunctional bridging ligands has proved to be a fertile field because of the intriguing network topologies and potential functions as new classes of materials. Currently, the rational design and synthesis of new extended supramolecular networks by both coordinative covalent and hydrogen-bonding interactions have resulted in a variety of such frameworks with fascinating structural motifs [3–5]. In general, extended networks possessing higher dimensionalities can be obtained by the assembly of coordination polymers with lower dimensionalities through hydrogen-bonding interactions and π–π

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stacking [6]. However, it is still a challenge to control the final products. For this, proper selection of metal ions and ligands is the key to design for self-assembly [7].

2,6-pyridinedicarboxylic acid is a good hydrogen-bond acceptor and can form strong hydrogen bonds and even hydrogen-bonded networks with H-donors. However, reports on metal-based 2,6-pyridinedicarboxylic acid containing supramolecular compounds are scarce, and cobalt metal-based supramolecular frameworks constructed from 2,6-pyridinedicarboxylic acid ligands have not yet been reported. In view of the excellent coordination capability of 2,6-pyridinedicarboxylic acid, we used 2,6-pyridinedicarboxylic acid as an organic building block to construct multidimensional supramolecular networks in the expectation that the group may generate covalent, hydrogen-bonding and/or π–π stacking interactions with transition metal ions in the assembly [8–13]. Herein we report the synthesis and structure of a novel compound, possessing unusual hydrogen-bonded and π–π stacking three-dimensional (3D) networks. To our knowledge, this compound represents the first metal-based supramolecular complex constructed from 2,6-pyridinedicarboxylic acid.

EXPERIMENTAL

Materials and General Methods

All reagents were available commercially and used as received. The C, H and N elemental analyses were performed on a Perkin-Elmer 2400 instrument. Co was determined by a Leaman inductively coupled plasma (ICP) spectrometer. FT-IR spectra were recorded as KBr pellets in the range 4000–400 cm^{-1} on an Alpha Centauri FT-IR spectrometer. An ESR spectrum was recorded at 298 K on a Japanese JES-FE3AX spectrometer.

Preparation of $(H_3O)_2[Cu(2,6\text{-pydc})_2]\cdot H_2O$ (1)

Pyridinedicarboxylic acid (0.085 g) was added to an aqueous solution of $CuCl_2\cdot 6H_2O$ (0.076 g) with stirring, and the resulting solution was adjusted to about pH 4.3 by addition of dilute HCl followed by further stirring for 30 min at room temperature. On evaporation, blue block-shaped single crystals were obtained after 5 days. Yield: 86% based on Cu. Anal. Calcd. for $C_{14}H_{14}N_2CuO_{11}$(%): C, 37.35; H, 3.11; Cu, 14.23; N, 6.22; O, 39.12. Found: C, 37.31; H, 3.10; Cu, 14.66; N, 6.21; O, 38.88.

X-ray Crystallography

A crystal of **1** with dimensions $0.453 \times 0.378 \times 0.317\,mm^3$ was selected for intensity data collection at 293 K on a Rigaku R-AXIS RAPID IP diffractometer with Mo Kα radiation. Empirical absorption corrections were applied. The structures were solved by direct methods and refined by a full-matrix least-squares technique based on F^2 using the program SHELXL 97 [14]. All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were located in difference Fourier maps. Data collection and refinement details are summarized in Table I. Selected bond distances and angles are given in Table II.

TABLE I Crystal data and refinement summary for complex **1**

Empirical formula	$C_{14}H_{14}N_2CuO_{11}$
Formula weight	449.8
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	13.454(3)
b (Å)	10.266(2)
c (Å)	13.783(3)
α (°)	90.00
β (°)	115.29(3)
γ (°)	90.00
V (Å^3)	1721.3(6)
Z	3
T (K)	293(2)
R_1	0.0423
wR_2	0.1217

TABLE II Selected bond lengths (Å) and angles (°) for compound **1**

Cu–N(1)	1.979(2)	Cu–O(7)	2.0792(18)
Cu–N(2)	1.909(2)	N(2)–C(13)	1.329(3)
Cu–O(4)	2.366(2)	C(1)–C(2)	1.509(4)
Cu–O(6)	2.053(2)	C(2)–C(3)	1.385(4)
Cu–O(2)	2.297(2)	C(3)–C(4)	1.378(4)
N(1)–Cu–N(2)	176.81(8)	N(1)–C(2)–C(3)	121.5(2)
N(1)–Cu–O(4)	75.28(8)	N(1)–C(2)–C(1)	116.9(2)
N(2)–Cu–O(4)	106.57(8)	C(3)–C(2)–C(1)	121.6(2)
N(1)–Cu–O(6)	102.23(8)	C(4)–C(3)–C(2)	119.4(2)
N(2)–Cu–O(6)	80.40(8)	C(3)–C(4)–C(5)	119.4(2)
O(4)–Cu–O(6)	91.96(8)	C(6)–C(5)–C(4)	118.3(2)
N(1)–Cu–O(2)	76.30(8)	N(1)–C(6)–C(5)	122.1(2)
N(2)–Cu–O(2)	101.91(8)	N(1)–C(6)–C(7)	114.5(2)
O(4)–Cu–O(2)	106.57(8)	C(5)–C(6)–C(7)	123.5(2)
C(1)–O(2)–Cu	112.23(16)	N(2)–C(9)–C(10)	120.1(2)
C(7)–O(4)–Cu	108.99(16)	N(2)–C(9)–C(8)	112.0(2)
C(8)–O(6)–Cu	113.98(16)	C(10)–C(9)–C(8)	127.9(2)
C(2)–N(1)–C(6)	121.5(6)	C(10)–C(11)–C(12)	120.4(2)
C(2)–N(1)–Cu	113.98(16)	C(13)–C(12)–C(11)	117.9(2)
C(6)–N(1)–Cu	120.80(16)	N(2)–C(13)–C(12)	117.9(2)
C(9)–N(2)–Cu	118.22(16)	C(12)–C(13)–C(14)	127.1(2)
C(13)–N(2)–Cu	119.22(16)	O(8)–C(14)–O(7)	126.3(2)
O(2)–C(1)–O(1)	127.2(3)	O(8)–C(14)–C(13)	118.5(2)
O(2)–C(1)–C(2)	114.9(2)	O(7)–C(14)–C(13)	115.2(2)
O(1)–C(1)–C(2)	117.9(3)		

RESULTS AND DISCUSSION

Structure of 1

The coordination environment of Cu(II) is shown in the ORTEP drawing in Fig. 1. Cu is equatorially coordinated to two 2,6-pyridinedicarboxylic acid ligands through their two nitrogen [Cu–N(1) 1.979(2) Å, Cu–N(2) 1.909(2) Å] and four oxygen atoms [Cu–O(2) 2.297(2) Å, Cu–O(6) 2.053(2) Å, Cu–O(4) 2.366(2) Å, Cu–O(7) 2.0792(18) Å]. The 2,6-pyridinedicarboxylic acid ligands lie approximately on the *ac*-planes and are

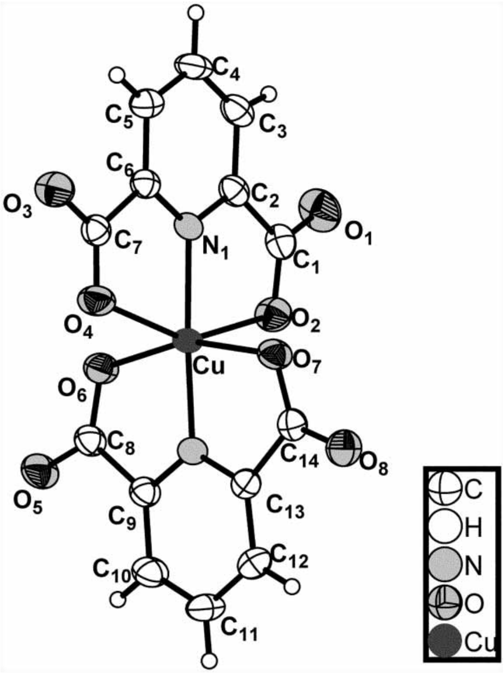

FIGURE 1. The asymmetric ucut of complex 1.

partially superimposed displaying π–π interactions and hydrogen bonds; the angle for donor–H–acceptor is 160.39°. A view of the unit cell along the *b*-axis is shown in Fig. 2. The 1D chain is linked by hydrogen bonds and the 1D chain is stacked approximately parallel to the *ac*-plane by π–π interactions to form 2D networks. The arrangement indicates π–π interactions between 2,6-pyridinedicarboxylic acid rings, forming 3D networks.

IR Spectroscopy

IR spectroscopy of solid complex **1**, in KBr pellets, was determined within the frequency range 4000–400 cm^{-1}. The main IR spectral data are shown in Fig. 3 and listed as follows $\nu_{O\text{–}H} = 3379, 3264, 3099$; $\nu_{C\text{–}O} = 1693$; $\nu_{PR} = 1629, 1477$ (PR = pyridine ring); $\delta_{OH} = 944$; $\delta_{C\text{–}H} = 1394, 841$; $\delta_{O\text{–}C\text{–}O} = 718$ (cm^{-1}).

The characteristic carboxyl vibrations in the free 2,6-pyridinedicarboxylic acid ligand are found at 1702 cm^{-1} as a strong and broad vibration and 1331 and 1299 cm^{-1} are assigned to the $\nu_{(C\text{–}O)}$ stretching vibrations [15,16].

The IR spectrum of **1** presents two distinguishable regions. High-energy bands, ranging from 3500 to 2700 cm^{-1}, show three absorption peaks due to $\nu_{O\text{–}H}$ of free water molecules. A series of absorption peaks are observed at lower energy, such as $\nu_{C\text{–}O}$ at 1693 cm^{-1}, ν_{PR} at 1629 and 1477 cm^{-1}, δ_{OH} at 944 cm^{-1}, and $\delta_{C\text{–}H}$ at 1394 and 841 cm^{-1}. The $\delta_{O\text{–}C\text{–}O}$ in-plane deformation vibration, which occurs as a strong sharp band at 701 cm^{-1} in the free H_2pdc ligand, shifts to 718 cm^{-1}, as found in the literature [16].

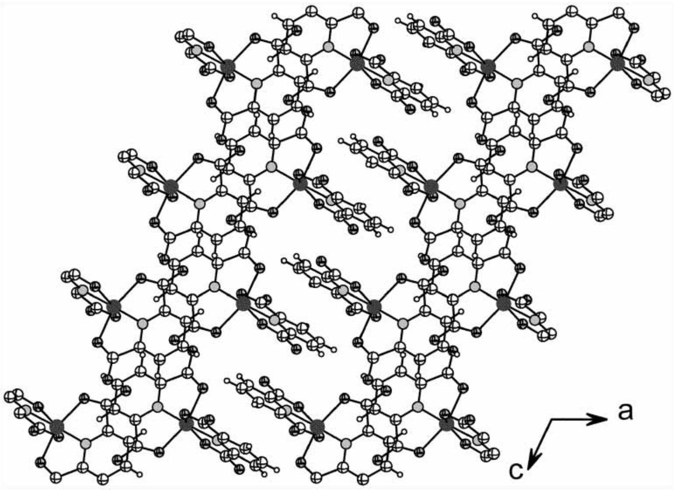

FIGURE 2. 2-D layered network in complex **1** in the *ac*-plane.

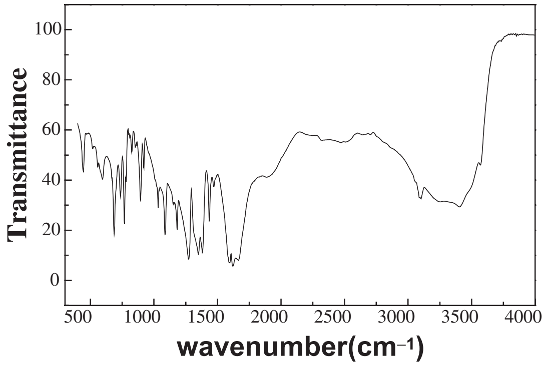

FIGURE 3. IR spectrum of complex **1**.

ESR Spectrum

The powder ESR spectrum of **1** at $-77\,K$ shown in Fig. 4 is typical for Cu^{2+} and gives $g = 2.310$.

CONCLUSIONS

In the present work, the synthesis of **1** demonstrates that pyridinedicarboxylic acid can provide multiple binding forces such as coordinate covalent, hydrogen-bonding and π–π stacking interactions for assembling multidimensional architectures. Furthermore, the use of the pyridinedicarboxylic acid group contributes new features to the rapidly expanding area of supramolecular chemistry. In summary, we provide here a possible

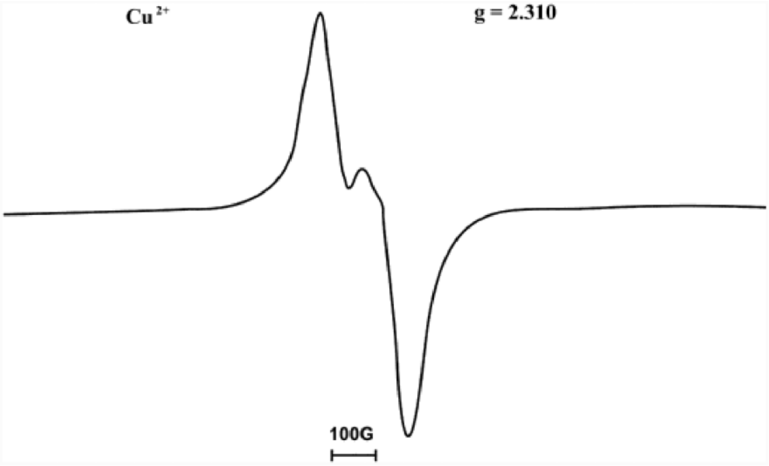

FIGURE 4. ESR spectrum of complex **1** at −77 K.

new strategy for the construction of coordination polymers. We are actively moving this strategy towards other related coordination polymers.

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