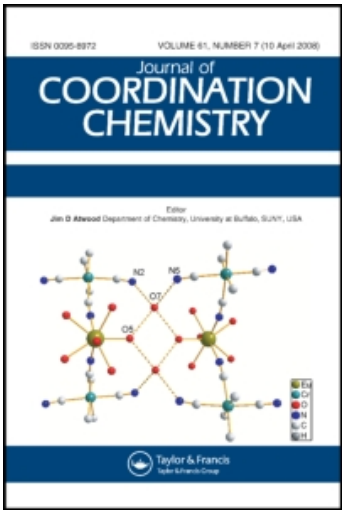

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Synthesis, crystal structure and magnetic properties of 2D bi-layered coordination polymer

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A new coordination polymer, $[Ni(pydc)(H_2O)_2]\cdot H_2O$ (**1**) (H_2pydc = pyridine-3,4-dicarboxylic acid), have been synthesized by treating Ni(II) nitrate with 3,4-pyridinedicarboxylic acid under hydrothermal conditions. The single-crystal X-ray structure reveals that **1** is a 2D bi-layered coordination polymer. Single-crystals are triclinic, space group $P\bar{1}$, with $a = 7.065(3)$, $b = 7.812(4)$, $c = 9.031(4)$ Å, $\alpha = 75.568(8)$, $\beta = 68.970(8)$, $\gamma = 75.927(8)^\circ$, $V = 444.0(3)$ Å^3, $Z = 2$. Variable temperature magnetic susceptibility measurements demonstrate a ferromagnetic interaction in **1**.

Keywords: Nickel; Pyridine-3,4-dicarboxylic acid; Crystal structure; Coordination polymer; Magnetic properties

1. Introduction

The design and construction of coordination polymers, a rapidly expanding field of crystal engineering [1], has attracted much attention due to their intriguing topologies [2] and potential applications as functional materials [3]. Many networks with various structural motifs, including honeycomb, brick wall, rectangular grid, bilayer, ladder, herringbone, diamondoid, and octahedral geometries [4–11], have been documented in the past decade. Polycarboxylate ligands exhibit various coordination modes to furnish various topologies [1b, 3c]. However, pyridine-3,4-dicarboxylic acid (H_2pydc) complexes have been little studied [12]. H_2pydc has several unique features with respect to *p*- and *m*-pyridine carboxylic acids. The two carboxyl groups are adjacent to each other and conjugation between pyridine and carboxyl groups is weak. Therefore, H_2pydc is likely to form high-dimensional frameworks with metal atoms [12a]. In this article, we reported the synthesis, crystal structure and magnetic properties of $[Ni(pydc)(H_2O)_2]\cdot H_2O$ (**1**).

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2. Experimental

2.1. *Materials and methods*

All reagents and solvents employed were commercially available and used as received without further purification. C, H, and N microanalyses were carried out with a Perkin-Elmer 240 instrument analyzer. FT-IR spectra (KBr pellets) were recorded in the 4000–400 cm^{-1} range on a Nicolet 5DX spectrophotometer. Variable-temperature magnetic susceptibility data were obtained using a Quantum Design MPMS-7SQUID magnetometer in the temperature range 2–300 K with an applied field of 10 kG.

2.2. *Synthesis*

A mixture of $Ni(NO_3)_2 \cdot 6H_2O$ (0.5 mmol), H_2pydc (0.5 mmol), NaOH (0.5 mmol) and H_2O (10 cm^3) was placed in a 23 cm^3 Teflon reactor and heated at 180°C for five days, then cooled to room temperature at a rate of 5 K h^{-1}. Green crystals of **1** were obtained in 80% yield. Anal. Calcd for $C_7H_9NNiO_7$ (%): C, 30.3; H, 3.3; N, 5.0. Found: C, 30.5; H, 3.1; N, 4.9. IR (cm^{-1}): 3293(vs), 1621(s), 1563(s), 1499(w), 1404(s).

2.3. *X-ray crystallography*

Single-crystal crystallographic data were collected at room temperature with a Bruker SMART Apex CCD area-detector diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using the ω scan mode. Data reduction and absorption corrections were performed with SAINT and SADABS software, respectively. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques using SHELXTL [13]. All non-hydrogen atoms were treated anisotropically. The positions of hydrogen atoms were generated geometrically. Crystallographic data and experimental details concerning the structure analysis are summarized in table 1. Selected bond lengths and angles are listed in table 2. The CCDC reference number for **1** is 244287.

3. Results and discussion

IR spectra of **1** show the absence of strong peaks around 1720 cm^{-1}, indicating that all carboxylic groups are deprotonated [14], consistent with the results of the X-ray analysis. Complex **1** is triclinic with one formula unit per asymmetric unit. The Ni(II) ion has octahedral geometry $\{NiNO_5\}$, being coordinated by four different pydc ligands (Ni1–O4 2.014(3) Ni1–N1A 2.063(3), Ni1–O1B Ni1–O1B 2.107(3), Ni1–O2C 2.183(3) Å) and two water molecules (Ni1–O1W 2.043(3), Ni1–O2W 2.083(3) Å) (figure 1a). Coordination modes of the pydc ligand in **1** are shown in figure 1(b). Each pydc ligand bonds to four Ni(II) ions, of which the pyridyl nitrogen atom and two *syn*-carboxylate oxygen atoms connect three Ni(II) centres to form a monolayer structure (figure 2a). One carboxylate group coordinates to Ni(II) through a single

Table 1. Crystallographic data for **1**.

Empirical formula	$C_7H_9NNiO_7$
Formula weight	277.86
Wavelength (Å)	0.70173
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	7.065(3)
b	7.812(4)
c	9.031(4)
α	75.568(8)
β	68.970(8)
γ	75.927(8)
V (Å^3)	444.0(3)
Z	2
D_c (g cm^{-3})	2.079
μ (mm^{-1})	2.21
$F(000)$	284
Crystal size (mm^3)	$0.04 \times 0.04 \times 0.01$
θ range for data collection (°)	2.46–28.26
Reflections collected	2726
Independent reflections (R_{int})	1925 (0.0173)
Max., min. transmission	0.974, 0.915
T (K)	293(2)
Data/restraints/parameters	1716/0/145
Final R indices [$I > 2\sigma(I)$][a]	$R_1 = 0.0421$
	$wR_2 = 0.1115$
R indices (all data)	$R_1 = 0.0480$
	$wR_2 = 0.1149$
Largest diff. peak and hole (e Å^{-3})	0.722, −0.808

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$; $wR_2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$.

Table 2. Selected bond distances (Å) and angles (°) for **1**.

Ni(1)–O(4)	2.014(3)	Ni(1)–O(1W)	2.043(3)
Ni(1)–N(1A)	2.063(3)	Ni(1)–O(2W)	2.083(3)
Ni(1)–O(1B)	2.107(3)	Ni(1)–O(2C)	2.183(3)
O(4)–Ni(1)–O(1W)	94.46(12)	O(4)–Ni(1)–N(1A)	97.01(13)
O(1W)–Ni(1)–N(1A)	93.12(12)	O(4)–Ni(1)–O(2W)	170.30(11)
O(1W)–Ni(1)–O(2W)	92.41(12)	N(1A)–Ni(1)–(2W)	89.43(12)
O(4)–Ni(1)–O(1B)	86.04(12)	O(1W)–Ni(1)–O(1B)	86.63(11)
N(1A)–Ni(1)–O(1B)	176.95(11)	O(4)–Ni(1)–O(2C)	88.25(11)

Symmetry transformations used to generate equivalent atoms are A: $x+1, y, z$; B: $x, y+1, z$; C: $-x+1, -y, -z+1$.

atom, and the other acts as a non-coplanar *syn–anti* O,O′-bridge connecting two Ni(II) centres; this results in a bilayered structure (figure 2b). The Ni···Ni distance in the Ni(OCO)Ni dimer present between two different monolayers is 4.664(3) Å while the shortest Ni···Ni distance in the monolayer is 7.065(3) Å (though pydc bridges).

Strong intermolecular hydrogen bonds exist between hydrogen atoms of the lattice water molecule and nearby carboxylate groups (O1W···O3W = 2.813(2) Å, ∠O1W–H···O3W = 101.8(1)°, O2W···O3W 2.785(2) Å, ∠O2W–H···O3W = 156.2(1)°, O1W···O3 = 2.784(2) Å, ∠O1W–H···O3 = 121.1(2)°). These interactions stabilize the free carboxylate groups in the structure.

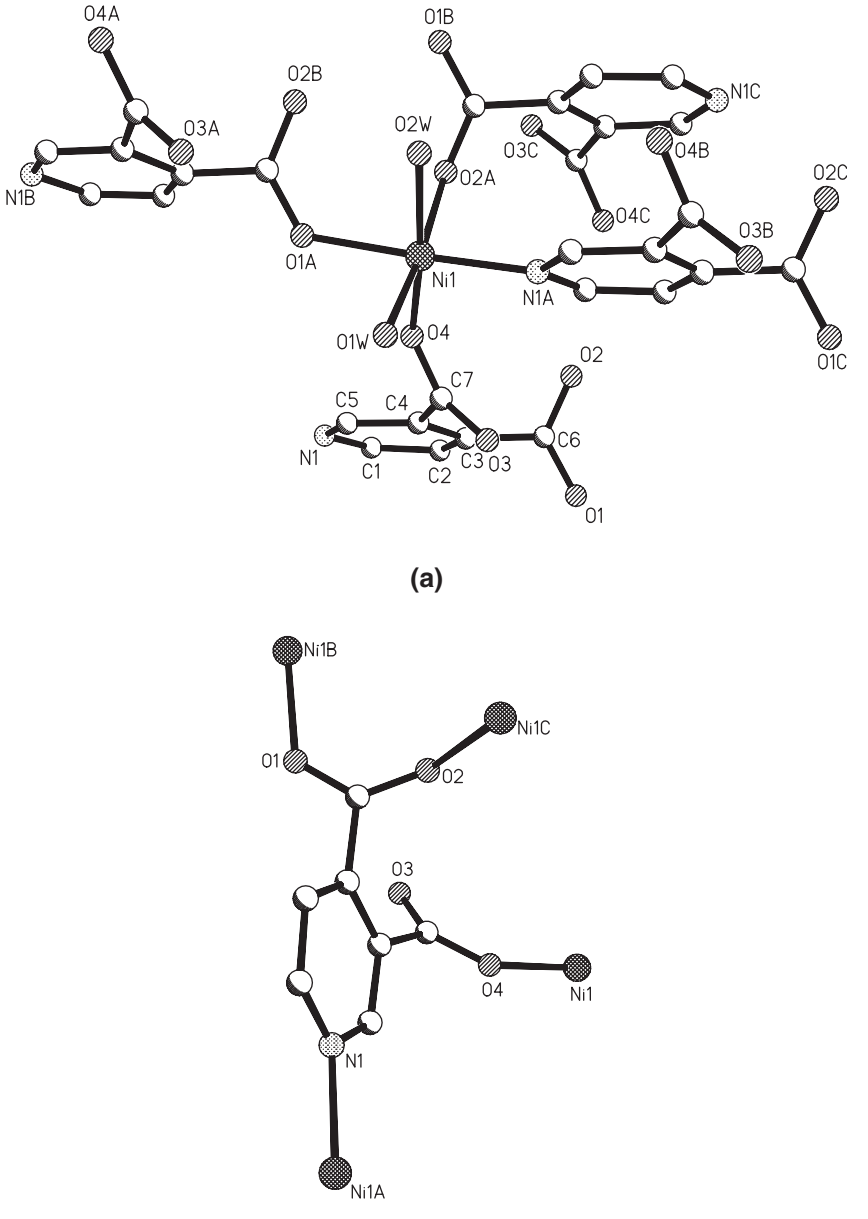

Figure 1. (a) Structure of **1** showing the atom numbering scheme; (b) the coordination modes of the pydc group.

Thermal variations of $\chi_m T$, and $1/\chi_m$ for **1** are shown in figure 3. The $\chi_m T$ value at room temperature is $1.28\,cm^3\,K\,mol^{-1}$ per Ni. Upon lowering the temperature, $\chi_m T$ gradually increases to $1.35\,cm^3\,K\,mol^{-1}$ at 16.0 K, showing a significant ferromagnetic interaction. Upon a further decrease of temperature, $\chi_m T$ decreases

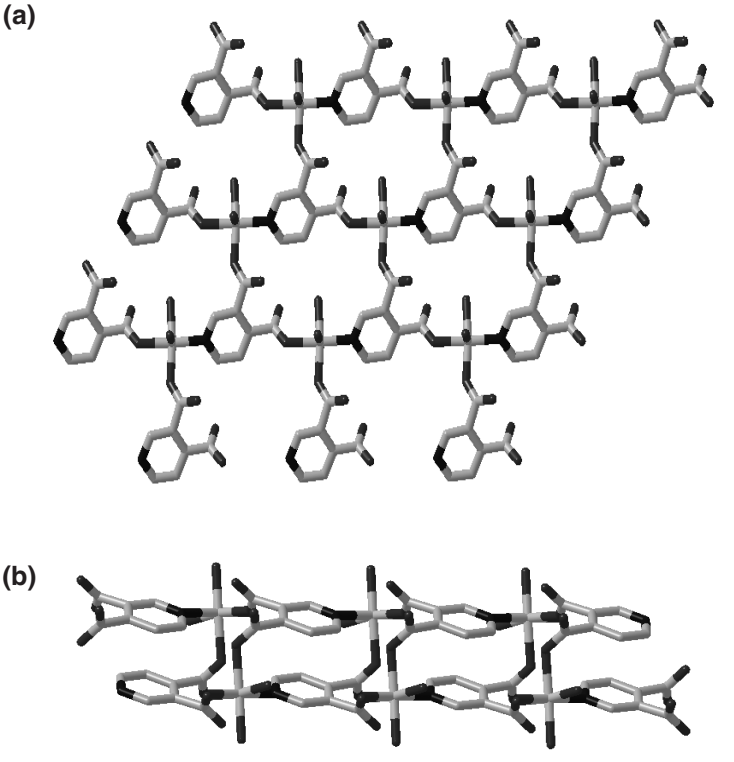

Figure 2. (a) A monolayer of the structure of **1** in the *ab* plane; (b) the bi-layered structure of **1** along the *a* axis.

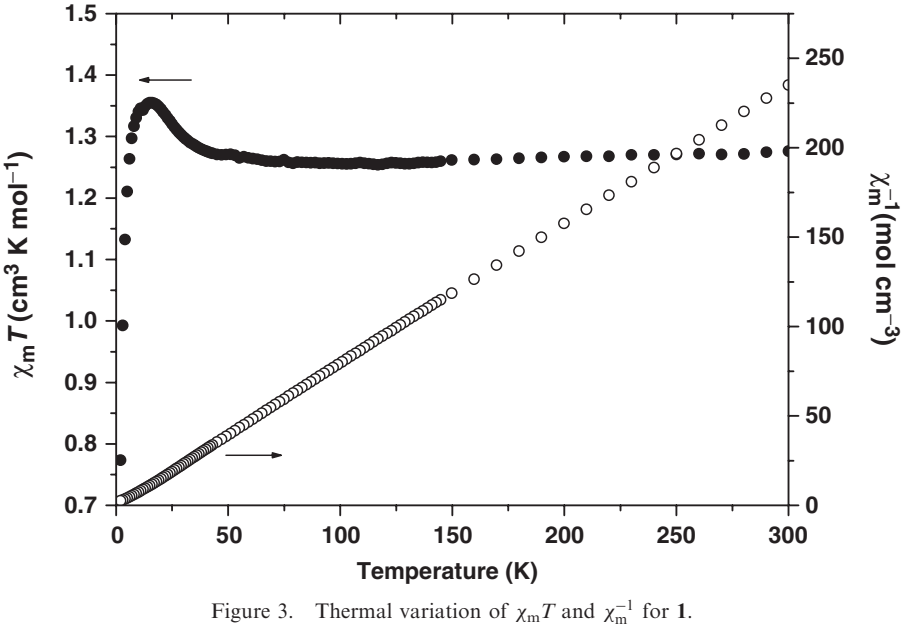

Figure 3. Thermal variation of $\chi_m T$ and χ_m^{-1} for **1**.

quickly due to the presence of zero-field splitting. The magnetic susceptibility obeys the Curie–Weiss law above 40 K with a Weiss constant $\theta = 0.94$ K, and a Curie constant $C = 1.26\,cm^3\,K\,mol^{-1}$, indicating significant ferromagnetic coupling between dimeric Ni(II) $S = 1$ spins through the *syn–anti* O,O′-bridges.

Supplementary material

Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int code +44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

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