

SHORT COMMUNICATION

SYNTHESIS AND CRYSTAL STRUCTURE OF TRANS-[Ni(pyzdch)₂(H₂O)₂] BASED ON PYRAZINE-2,3-DICARBOXYLIC ACID

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ABSTRACT. The determined structure of the title compound C₂₄H₂₀Ni₂N₈O₂₀ consists of the mononuclear *trans*-[Ni(pyzdch)₂(H₂O)₂], (pyzdch = pyrazine-2,3- dicarboxylate). The Ni(II) atom is hexa-coordinated by two (pyzdch)⁻ groups and two water molecules. The coordinated water molecules are in *trans*-diaxial positions and the (pyzdch)⁻ anion acts as a bidentate ligand through an O atom of the carboxylate group and the N atom of the pyrazine ring. There are diverse hydrogen bonding interactions such as O—H...N and O—H...O contacts, which lead to the formation of a three-dimensional supramolecular architecture.

KEY WORDS: Ni(II), Pyrazine-2,3-dicarboxylic acid, Coordination chemistry, Supramolecular chemistry, Hydrogen bond, Proton transfer

INTRODUCTION

Crystal engineering and supramolecular chemistry is a rapidly expanding area of solid-state chemical research for its versatile applications [1]. Crystal engineering exploits hydrogen bond and other non-covalent directional interaction to design and synthesize new compound with specific properties [2, 3]. Among the intermolecular interactions hydrogen bonding interaction plays an important role in determining molecular conformation and supramolecular aggregation of molecules [4]. In simpler expression it can be stated that supramolecular architecture is built up by different hydrogen bonding interaction. So, organic ligands and aromatic molecules have been studied extensively in the crystal structure to assemble supramolecular network organized by coordination bonds, hydrogen bonds and π - π stacking interaction [5]. As one of these ligands, the dicarboxylate ligand, pyzdch₂ has drawn extensive attentions [6-15]. Metal pyrazine dicarboxylate complexes can construct versatile structural motifs, which generate various supramolecular architectures with interesting properties. After our previous works on synthesizing coordination compounds *via* proton transfer mechanism [10-15] including copper, manganese, cobalt and zinc atom herein, we planned the reaction between pyzdch₂, piperazine, and nickel(II) chloride in order to provide a new proton transfer compound.

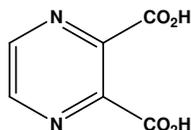
EXPERIMENTAL

Pyzdch₂ acid and pipz were purchased from Merck Company. The X-ray data was obtained with a Bruker SMART CCD diffractometer.

Preparation of [Ni(pyzdch)₂(H₂O)₂]. A solution of pyzdch₂ (0.18 mmol, 0.03 g) and piperazine (0.023 mmol, 0.02 g) in water (10 mL) refluxed for 1 h, then a solution of

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$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.02 mmol, 0.01 g) was added dropwise and continued refluxing for 6 h at 60 °C. The obtained green solution gave green block like crystals of title compound after several months with slow evaporation of solvent at R.T.



Pyrazine-2-3-dicarboxylic acid.

Molecular and crystal structure of the title compound. The crystallographic data of the title compound is given in Table 1, the selected bond lengths and angles and torsion angles are shown in Table 2 and the hydrogen bond geometry is shown in Table 3. The result showed that the piperazine did not play any role at the reaction, neither as a counter ion, nor as a ligand and the final product was $[\text{Ni}(\text{pyzdcH})_2(\text{H}_2\text{O})_2]$ as shown in Figure 1. The crystal packing diagram of the title compound is also rendered in Figure 2. The equatorial plane is occupied by two $(\text{pyzdcH})^-$ ligands coordinated through their pyridine nitrogen atoms and one of the deprotonated carboxylate group oxygen atoms. The two coordinated water molecules occupy axial positions. This compound consists of one natural moiety, *trans*- $[\text{Ni}(\text{pyzdcH})_2(\text{H}_2\text{O})_2]$ complex. The existence of the classical hydrogen bonding causes the complex molecules connected to each other and thus a supramolecular structure will be formed.

Table 1. Crystal data and refinement parameters for **1**.

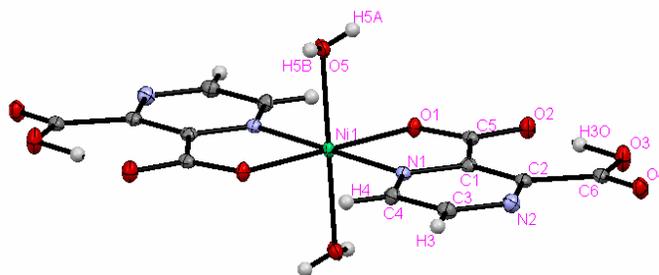
Empirical formula	$\text{C}_{24}\text{H}_{20}\text{Ni}_2\text{N}_8\text{O}_{20}$
Formula weight	857.90
Temperature (K)	120 (2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group, unit cell	$P2(1)/n$ $Z = 1$
Unit cell dimensions	$a = 9.2595(5)$ Å $b = 7.6554(4)$ Å $c = 9.9997(5)$ Å $\alpha = 90.0$ $\beta = 94.071(5)^\circ$ $\gamma = 90.0^\circ$
Unit cell volume (Å ³)	707.05 (8)
Absorption coefficient (mm ⁻¹)	1.45
$F(000)$	436
Theta range for data collection	3.1 to 27.6°
Index range	$-10 \leq h \leq 11$, $-9 \leq k \leq 5$, $-10 \leq l \leq 11$
Reflection collected	2886
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.03
Final R indices [$I > 2.0 \sigma(I)$]	$R1 = 0.0189$, $wR2 = 0.029$
R indices (all data)	$R1 = 0.0214$, $wR2 = 0.0536$

Table 2. Selected bond distances, bond angles and torsion angles for **1**.

Ni1—O1	2.0248(11)	O2—H3O	1.26(3)
Ni1—O5	2.0863(12)	O3—H3O	1.16(3)
Ni1—N1	2.0434(13)	O1—C5	1.2458(19)
Ni1—O4	2.5167 (6)	O2—C5	1.2577(19)
O3—C6	1.295 (2)	O4—C6	1.2184(19)
O1—Ni1—O1 ⁱ	180.00 (6)	O1 ⁱ —Ni1—O5 ⁱ	88.14 (5)
O1—Ni1—N1	79.65 (5)	N1—Ni1—O5 ⁱ	91.24 (5)
O1 ⁱ —Ni1—N1	100.35 (5)	N1 ⁱ —Ni1—O5 ⁱ	88.76 (5)
O1—Ni1—N1 ⁱ	100.35 (5)	O1—Ni1—O5	88.14 (5)
O1 ⁱ —Ni1—N1 ⁱ	79.65 (5)	O1 ⁱ —Ni1—O5	91.86 (5)
N1—Ni1—N1 ⁱ	180.00 (6)	N1—Ni1—O5	88.76 (5)
O1—Ni1—O5 ⁱ	91.86 (5)	N1 ⁱ —Ni1—O5	91.24 (5)
O5 ⁱ —Ni1—O5	180.000 (1)		
O1 ⁱ —Ni1—N1—C1	-178.80(10)	N1 ⁱ —Ni1—N1—C1	-77(100)
O1—Ni1—N1—C1	1.20(10)	Ni1—N1—C1—C5	-0.81(15)
O5 ⁱ —Ni1—N1—C1	92.87(11)	Ni1—N1—C1—C2	179.24(11)
O5—Ni1—N1—C1	-87.13(11)	Ni1—N1—C4—C3	-179.85(11)

Symmetry codes: (i) $-x+1, -y+1, -z+1$.Table 3. The geometry of intra- and intermolecular interactions in **1**.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H5A \cdots O4 ⁱⁱ	0.69(2)	2.12(2)	2.8013(19)	174(2)
O5—H5B \cdots O4 ⁱⁱⁱ	0.88(3)	2.06(3)	2.9225(18)	166(2)
O5—H5B \cdots N2 ⁱⁱⁱ	0.88(3)	2.64(2)	3.252(2)	127.3(19)
O3—H3O \cdots O2	1.16(3)	1.26(3)	2.4103(16)	171(3)

Symmetry codes: (ii) $x-1, y, z$; (iii) $-x+3/2, y-1/2, -z+1/2$.Figure 1. Molecular structure of $[\text{Ni}(\text{pyzdc})_2(\text{H}_2\text{O})_2]$ complex. Ellipsoids are drawn at the 50% probability level.

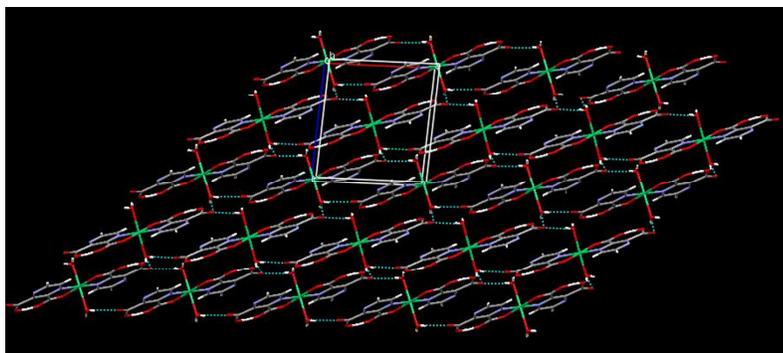


Figure 2. Packing diagram of $[\text{Ni}(\text{pyzdc})_2(\text{H}_2\text{O})_2]$ complex in *b*-direction. Hydrogen bonds are shown as dashed lines.

Supplementary data. CCDC 810429 contains the crystallographic data for the structure has been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail for deposition: deposit@ccdc.cam.ac.uk).

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