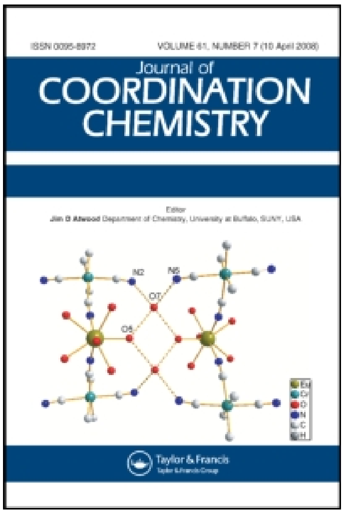

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A nickel 1-D zigzag chain coordination polymer of 2-pyrazinecarboxylic acid

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A nickel 1-D zigzag chain coordination polymer of 2-pyrazinecarboxylic acid

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$[Ni(pyza)_2H_2O]_n$ has been synthesized by hydrothermal reaction of 2-pyrazinecarboxylic acid (Hpyza) and $Ni(CH_3COO)_2 \cdot 4H_2O$ in the presence of 1,10-phenanthroline and structurally characterized by elemental analysis, IR, UV and single crystal X-ray diffraction. The title complex displays an infinite zigzag chain structure in which each nickel(II) center is coordinated by three nitrogen and three oxygen atoms to generate a NiN_3O_3 octahedral geometry. The existence of hydrogen bond leads to formation of the interpenetrating stacked structure.

Keywords: Hydrothermal synthesis; Nickel coordination polymer; Crystal structure

1. Introduction

Transition metal-organic frameworks (MOFs) attract attention for their applications in catalysis, co-operative magnetic behavior, non-linear optical activity, electrical conductivity and to their interesting topologies [1–8]. The selection of organic ligands with appropriate coordination sites is key to formation of MOFs with desirable physical and chemical properties. Carboxylic acids, as well as carboxylates, form various coordination complexes due to its diverse coordination modes. 2-pyrazinecarboxylic acid, containing two nitrogen heteroatoms in *ortho*- and *meta*-positions of the benzene ring, is a versatile ligand that can bind metal ions in a variety of bonding modes [9–11]. The two nitrogen atoms and the two carboxylic oxygen atoms can act as donor atoms, capable of participating in strong coordination bonds, oriented in various directions. At the same time the oxygen and the nitrogen atoms can also play roles as hydrogen bond acceptors, driving the formation of supramolecular assemblies [12–13].

Hydrothermal synthesis has been employed to obtain single crystals and has been applied in the syntheses of a large number of transition metal complexes with one-dimensional chain-like, two-dimensional layer-like or three-dimensional net-like open framework structures [14–18]. We chose 2-pyrazinecarboxylic acid and o-phenanthroline as the reactants to synthesize nickel ternary complex under hydrothermal conditions. We did not get a ternary complex, but the nickel binary complex, which shows a zigzag chain structure [19].

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2. Experimental

2.1. *Materials and methods*

$Ni(CH_3COO)_2 \cdot 4H_2O$ and 2-pyrazinecarboxylic acid were purchased from Aldrich and used without further purification. All other reagents were commercially available and used as received. Elemental analyses (C, H, N) were determined on an Elementar Cario EL elemental analyzer. Infrared spectroscopy on KBr pellets was performed on a Nexus 912 AO446 FT-IR spectrophotometer in the 4000–400 cm^{-1}. Ultraviolet absorption spectra were measured using an Agilent 8453 spectrophotometer between 200 and 400 nm (in water).

2.2. *Preparation of the title complex*

$Ni(CH_3COO)_2 \cdot 4H_2O$(74.7 mg, 0.3 mmol), 2-pyrazinecarboxylic acid(74.5 mg, 0.3 mmol) and 1,10-phenanthroline (59.5 mg, 0.3 mmol) were mixed in 5 mL deionized water. After stirring 30 min, the mixture was placed in a 15 mL Teflon-lined reactor and heated at 160°C in an oven for 3d, then slowly cooled to room temperature. Dark blue diamond crystals of the title complex suitable for X-ray diffraction analysis were obtained. Anal. Calcd for $C_{10}H_8N_4NiO_5$(322.91): C, 37.16; H, 2.48; N, 17.34%. Found: C, 38.03; H, 2.53; N, 17.22%.

2.3. *X-ray crystallography*

Diffraction data for a crystal with dimensions $0.10 \times 0.08 \times 0.06\,mm^3$ for the complex were performed with graphite-monochromated Mo-Kα radiation on a CCD area detector four-circle diffractometer, and were collected by the ω-2θ scan technique. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. The hydrogen atoms were added geometrically and not refined. All calculations were performed using SHELXS−97 and SHELXL−97 [20, 21]. A summary of crystallographic data and refinement parameters is given in table 1. Crystallographic data for the complex is deposited at the Cambridge Crystallographic Data Center CCDC, the deposition number is CCDC 613550.

3. Results and discussion

IR spectrum of the complex displays a broad band at 3199 cm^{-1}, corresponding to the O–H stretching vibration of coordinated water. The peak at 1668 cm^{-1} is attributed to ν(C=O) of carboxylate of Hpyza as is 1336 cm^{-1} consistent with carboxylate of Hpyza coordinating monodentate to Ni (II).

The UV/vis absorption spectra for free Hpyza ligand and its nickel complex in water are compared. For free Hpyza ligand, there is a strong absorption band in the range of 200–300 nm and the absorption maximum at 267 nm is associated with $\pi \rightarrow \pi^*$ transitions in the aromatic rings [22]. This absorption band for the nickel complex decreases and exhibits a slight blue shift (at about 269 nm) compared with that of free

Table 1. Crystal data and structure refinement for the complex.

Complex	$[Ni(pyza)_2 \cdot H_2O]_n$
Formula	$C_{10}\ H_8\ N_4\ Ni\ O_5$
Relative molecular mass M_n	322.91
Color	Blue
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Radiation	Mo-Kα
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit dimensions (Å, °)	
a	7.778(2)
b	9.849(3)
c	14.891(4)
β	90
Volume ($Å^3$)	1140.7(5)
Z	4
Calcd density ($Mg\,m^{-3}$)	1.880
Absorption coefficient (mm^{-1})	1.729
$F(000)$	656
Crystal size (mm^3)	$0.10 \times 0.08 \times 0.06$
θ range for data collection (°)	2.48 to 27.01
Reflections/collected/unique	5711/2460 [$R_{(int)} = 0.0359$]
Completeness to $2\theta = 26.00$	99.9%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9034 and 0.8461
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2460/3/190
Goodness-of-fit on F^2	0.950
Final R indices [$I > 2(I)$]	$R_1 = 0.0272$, $wR_2 = 0.0516$
Largest diff. peak and hole ($e\,Å^{-3}$)	0.372 and −0.250

Hpyza ligand, suggesting that the coordination interaction between the nickel ion and Hpyza makes the complex form the more extensive $\pi \rightarrow \pi^*$ conjugated system. In addition, a weaker absorption band could be observed at 309 nm for free Hpyza ligand that can be assigned to the $n \rightarrow \pi^*$ transition of the nonbonding electrons of the heterocyclic nitrogen atoms [22]. However, there is no absorption band in the range of 300–400 nm for the nickel complex, which implies that the heterocyclic nitrogen atoms participate in coordination. There exist very weak absorption bands between 500 to 800 nm, which can be ascribed to the d–d transitions of nickel (II).

Figure 1 shows the coordination geometry and atom labeling in the crystal structure of $[Ni(pyza)_2(H_2O)]_n$. The title complex crystallizes in orthorhombic with an asymmetric unit consisting of one formula unit and therefore there is only one metal environment. The coordination environment of nickel(II) displays a distorted octahedral coordination geometry with three nitrogen atoms and two oxygen atoms from three different Hpyza ligands and another oxygen from water in the apical position. Two oxygens (O(2) and O(3)) of carboxylate groups and their adjacent nitrogen (N(1) and N(4)) donors of chelating Hpyza ligands occupy the basal plane and another nitrogen atom (nonchelated N(3)) of Hpyza ligand bonds to nickel(II) in an apical position to form an infinite zigzag structure through Ni–N(3) bond. The dihedral angle of two chelating pyza ligands is 8.8°. The coordination environment of Ni(II) in the title complex is different from the coordination sphere of Ni(II) reported in the

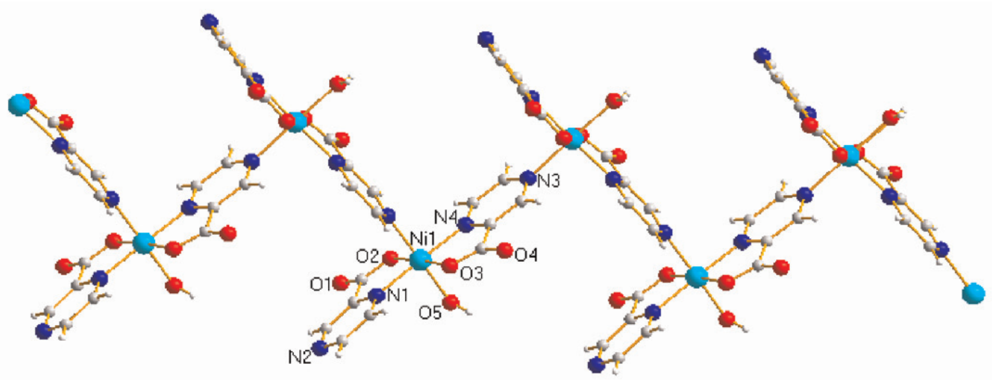

Figure 1. View of the one-dimensional chains in **1**, showing the {NiN_2O_4} coordination sphere of Ni ions.

Table 2. Selected bond distances (Å) and angles (°) for the complex.

Ni(1)–O(2)	2.0336(19)	Ni(1)–N(1)	2.071(2)
Ni(1)–O(3)	2.0294(18)	Ni(1)–N(4)	2.086(2)
Ni(1)–O(5)	2.0567(18)	Ni(1)–N(3)#1	2.120(2)
O(3)–Ni(1)–O(2)	175.71(7)	O(3)–Ni(1)–N(3)#1	94.08(7)
O(3)–Ni(1)–O(5)	89.47(8)	O(2)–Ni(1)–N(3)#1	89.10(8)
O(2)–Ni(1)–O(5)	87.36(8)	O(5)–Ni(1)–N(3)#1	176.44(9)
O(3)–Ni(1)–N(1)	96.70(8)	N(1)–Ni(1)–N(3)#1	90.97(8)
O(2)–Ni(1)–N(1)	80.35(8)	N(4)–Ni(1)–N(3)#1	89.55(8)
O(5)–Ni(1)–N(1)	88.76(8)	C(5)–O(2)–Ni(1)	116.08(18)
O(3)–Ni(1)–N(4)	80.76(8)	C(10)–O(3)–Ni(1)	116.15(16)
O(2)–Ni(1)–N(4)	102.16(8)		
O(5)–Ni(1)–N(4)	90.87(8)		

Symmetry transformations used to generate equivalent atoms: #1: $-x$, $y+1/2$, $-z+3/2$.

literature [19], in which the metal centre lies in a distorted octahedral coordination environment {NiN_2O_4}, consisting of two nitrogen donors from two pyrazine rings and two oxygen donors from two monodentate carboxylic acid groups and the other two oxygen donors from two coordinated waters in the apical positions.

Selected bond lengths and angles are listed in table 2. The distances of Ni–O (O(2), O(3) and O(5)) and Ni–N (N(1), N(3) and N(4)) range from 2.0294(18) to 2.0567(18) and from 2.071(2) to 2.120(2) Å, respectively. The Ni–O distances (from chelating pyza ions) are shorter than that of Ni–O (from coordinated water) and the distances of Ni–N (from chelating pyza ions) are shorter than that of Ni–N (from bridging pyza ion). The O(2)– Ni–O(3) and N(1)– Ni–N(4) bond angles are 175.71(7)° and 177.44(9)°, respectively. The N(3)–Ni–O(5) angle is 176.44(9)°.

The Hpyza ligands adopt two coordination modes; bidentate-chelating (figure 2(a)), and tridentate-bridging (figure 2(b)) which is not observed in the previous structure [19]. Oxygen of carboxylate and its adjacent nitrogen atom coordinate to central nickel(II) to form a five-membered chelating ring. Furthermore, the two types of Hpyza ligands play different roles in construction of the resulting architecture. The terminal units make no contribution to the extension of chains but instead extend outward on opposite sides of

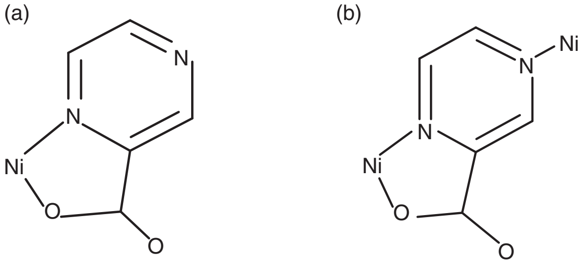

Figure 2. The coordination modes of Hpyza ligand.

Table 3. Hydrogen bonds (Å, °) for the complex.

D–H···.A	*d*(D–H)	*d*(H···A)	*d*(D···A)	*d*(DHA)
O(5)–H(5A)...O(2)#3	0.839(10)	1.844(11)	2.678(3)	173(3)
O(5)–H(5B)...O(3)#4	0.826(10)	1.948(12)	2.754(3)	165(3)

Symmetry transformations used to generate equivalent atoms: #1: $-x$, $y+1/2$, $-z+3/2$; #2: $-x$, $y-1/2$, $-z+3/2$; #3: $x+1/2$, $-y+3/2$, $-z+2$; #4: x$-1/2$, $-y+3/2$, $-z+2$.

the chains; whereas the bridging Hpyza ligands connect adjacent nickel ions into a zigzag chain structure.

There are two types of O–H···O intermolecular hydrogen bonds in the unit cell of the title complex: O(5)–H···O(2) and O(5)–H···O(3) (figure 3); they are both hydrogen bonds between oxygens of coordinated water and of chelating pyza ion. The detailed data of hydrogen bonds are shown in table 3. The weak interaction of the hydrogen bonds between adjacent zigzag chains leads to the formation of a two-dimensional interpenetrating structure (figure 3).

1,10-Phenanthroline was introduced into reaction system as a building block to bridge between nickel atoms to give an open framework. However, phen was not a ligand in the system and we obtained a coordination polymer with 1D zigzag chain structure, which was different from the previously reported structure [19]. In the previously reported structure, only bidentate-chelating coordination mode of Hpyza ligands was observed, while in the title complex, both bidentate-chelating and tridentate-bridging coordination modes of Hpyza ligands coexist. Experiments without phen did not give rise to the title compound but the previously reported structure, which suggests that although phen does not function as a ligand, the presence of phen is important to the synthesis of the title complex. The effect of auxiliary ligands such as phen on the MOFs system is currently under study.

4. Conclusion

In summary, we have obtained a new 1D zigzag chain complex by assembling $Ni(CH_3COO)_2 \cdot 4H_2O$ with 2-pyrazinecarboxylic acid (Hpyza) in the presence of 1,10-phenanthroline. The structure is different from the previously reported complex,

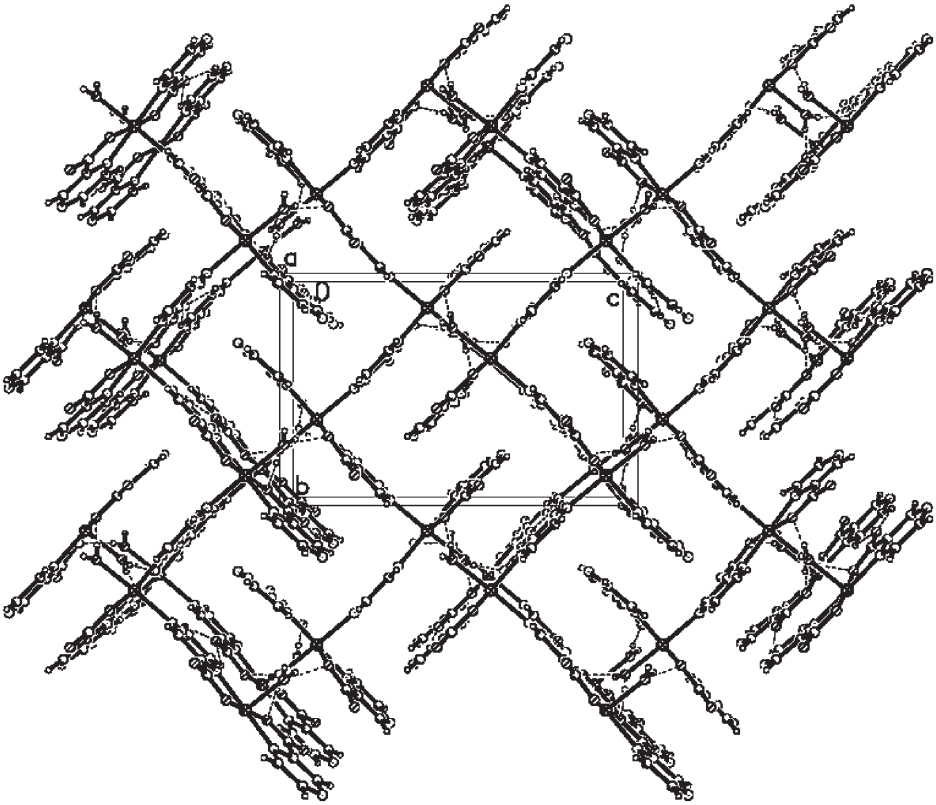

Figure 3. Packing view of the unit cell for the complex.

which shows the influence of an auxiliary ligand such as phen on the structure of the complex.

Acknowledgements

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