

## 苯四甲酸桥连的镍配合物 [Ni(btec)(H<sub>2</sub>O)<sub>4</sub>][Ni(im)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]·2H<sub>2</sub>O 的合成及结构

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### Synthesis and Structure of a 1,2,4,5-benzenetetracarboxylato-bridged Nickel Complex [Ni(btec)(H<sub>2</sub>O)<sub>4</sub>][Ni(im)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]·2H<sub>2</sub>O

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**Abstract:** At room temperature, a coordination polymer [Ni(btec)(H<sub>2</sub>O)<sub>4</sub>][Ni(im)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]·2H<sub>2</sub>O was synthesized by reaction of NiCl<sub>2</sub>·6H<sub>2</sub>O, 1,2,4,5-benzenetetracarboxylic dianhydride and imidazole in a water/THF solution. The structure was determined by X-ray diffraction crystal structure analysis. It crystallizes in triclinic  $P\bar{1}$  space group with the crystal cell parameters of  $a=0.675\ 42\ (2)\ \text{nm}$ ,  $b=1.000\ 14\ (1)\ \text{nm}$ ,  $c=1.090\ 88\ (3)\ \text{nm}$ ,  $\alpha=74.140(2)^\circ$ ,  $\beta=74.388(1)^\circ$ ,  $\gamma=73.239(2)^\circ$ , and  $V=0.664\ 09(3)\ \text{nm}^3$ ,  $Z=1$ . The crystal structure shows that Ni1 atom is coordinated by four water and two imidazole molecules, while Ni2 is coordinated by four water molecules and two carboxyl oxygen atoms. The 1,2,4,5-benzenetetracarboxylate ions bridge Ni2 coordination centers to form one-dimensional chain structure. Moreover, the chains are further linked together by hydrogen bonds to form a two-dimensional network. CCDC: 295873.

**Key words:** 1,2,4,5-benzenetetracarboxylate; nickel; crystal structure

The design and synthesis of metal-organic coordination polymers have rapidly developed in recent years. Multi-carboxylate ions have attracted much attention because of the diversity of the binding modes of the carboxylate groups. So far a larger number of metal coordination polymers have been isolated by using the multi-carboxylic acid ligands, for example, 1,2,4,5-benzenetetracarboxylic acid (H<sub>4</sub>btec)<sup>[1-3]</sup>, 1,3,5-benzenetricarboxylic acid (H<sub>3</sub>btc)<sup>[4-6]</sup>, and 1,4-benzenedi-

carboxylic acid (*p*-H<sub>2</sub>bdc)<sup>[7-9]</sup>. In this work, we present the synthesis and structural characterization of a new nickel coordination polymer [Ni(btec)(H<sub>2</sub>O)<sub>4</sub>][Ni(im)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]·2H<sub>2</sub>O, where the imi stands for the neutral molecule of imidazole.

## 1 Experimental

### 1.1 Reagent and apparatus

All chemicals were of analytical reagent grade and

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were used directly without further purification. Elemental analysis (C, H, N) was performed with a Vario EL III CHNOS Elemental Analyzer. IR spectrum was recorded from KBr pellets in the range of  $4\,000 \sim 400\text{ cm}^{-1}$  on a FTS-40 spectrophotometer.

## 1.2 Synthesis

A mixture of 1,2,4,5-benzenetetracarboxylic dianhydride (0.25 g, 1.15 mmol), imidazole (0.23 g, 3.38 mmol),  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.25 g, 1.05 mmol) and  $\text{H}_2\text{O}/\text{THF}$  (3/1, 20 mL) was stirred for 30 min. The resulting solution was allowed to stand at ambient temperature without further disturbing for two weeks or so to give green crystals. Anal. calcd for  $\text{C}_{16}\text{H}_{30}\text{N}_4\text{Ni}_2\text{O}_{18}$  (%): C, 28.1; H, 4.42; N, 8.19. Found (%): C, 27.57; H, 4.31; N, 8.31. IR (KBr): 3 371(s), 1 597(s), 1 489(m), 1 433(m), 1 383(s), 1 327(m), 1 169(s), 1 099(m), 1 070(s), 920(w), 845(m), 791(w), 748(w), 687(m), 663(m), 615(m)  $\text{cm}^{-1}$ .

## 1.3 Crystal structure determination

A green single crystal with dimensions of 0.20 mm

$\times 0.16\text{ mm} \times 0.08\text{ mm}$  was selected for structure determination. The data collection was performed on Siemens SMART CCD diffractometer equipped with graphite monochromated Mo  $K\alpha$  radiation ( $\lambda=0.071\,073\text{ nm}$ ) at room temperature. Cell parameters were determined by the least-squares calculations with  $\theta$  angles ranging from  $1.98^\circ$  to  $25.06^\circ$ . A total of 3 394 independent reflections were collected and 2 270 reflections were independent ( $R_{\text{int}}=0.038\,4$ ), of which 1 973 were observed with  $I>2\sigma(I)$ . An empirical absorption correction was applied using SADABS<sup>[10]</sup>. The structure was solved by direct method and refined on  $F^2$  by full-matrix least-square using the SHELX-97 program package<sup>[11]</sup>, giving a final  $R_1=0.067\,2$ ,  $wR_2=0.148\,8$ . The largest peak and hole on the final difference-Fourier map were 711 and  $-541\text{ e} \cdot \text{nm}^{-3}$ , respectively. Crystal data and structure refinement parameters are listed in Table 1. Selected bond lengths and angles are given in Table 2.

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Table 1 Crystal data and structure refinement for  $[\text{Ni}(\text{btcc})(\text{H}_2\text{O})_4][\text{Ni}(\text{imi})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$

Molecule formula	$\text{C}_{16}\text{H}_{30}\text{N}_4\text{Ni}_2\text{O}_{18}$	$V / \text{nm}^3$	0.664 09(3)
Molecule weight	683.86	$Z$	1
Crystal size / mm	$0.20 \times 0.16 \times 0.08$	$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.71
Crystal color	Green	$F(000)$	354
Crystal system	Triclinic	Goodness of fit on $F^2$	1.181
Space group	$P\bar{1}$	Data / restraints / parameters	2 270 / 8 / 225
$a / \text{nm}$	0.675 42(2)	Absorption coefficient / $\text{mm}^{-1}$	1.507
$b / \text{nm}$	1.000 14(1)	Absorption correction $T_{\text{max}} / T_{\text{min}}$	0.886 / 0.735
$c / \text{nm}$	1.090 88(3)	Largest diff. peak and hole / ( $\text{e} \cdot \text{nm}^{-3}$ )	0.711 / $-0.541$
$\alpha / (^\circ)$	74.140(2)	$R_1, wR_2 [I>2\sigma(I)]$	0.067 2, 0.148 8
$\beta / (^\circ)$	74.388(1)	$R_1, wR_2$ (all data)	0.082 4, 0.187 7
$\gamma / (^\circ)$	73.239(2)		

Table 2 Selected bond lengths (nm) and angles ( $^\circ$ ) for  $[\text{Ni}(\text{btcc})(\text{H}_2\text{O})_4][\text{Ni}(\text{imi})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$

Ni(1)-O(2)	0.205 1(7)	Ni(1)-O(1)	0.210 9(7)	Ni(2)-O(6)	0.205 0(6)
Ni(1)-N(1)	0.206 3(8)	Ni(2)-O(4)	0.203 7(5)	Ni(2)-O(5)	0.2091 (6)
O(2)-Ni(1)-N(1)	90.6(3)	N(1)-Ni(1)-O(1)	89.7(3)	O(4)-Ni(2)-O(5)	88.6(2)
O(2)-Ni(1)-O(1)	86.8(3)	O(4)-Ni(2)-O(6)	86.9(2)	O(6)-Ni(2)-O(5)	92.5(3)

## 2 Results and discussions

The crystal structure of the title complex consists of discrete  $[\text{Ni}(\text{imi})_2(\text{H}_2\text{O})_4]^{2+}$  cations, polymeric  $[\text{Ni}(\text{btcc})(\text{H}_2\text{O})_4]^{2-}$  anions and lattice water molecules. A locally

expanded unit of the title complex is shown in Fig.1. In  $[\text{Ni}(\text{imi})_2(\text{H}_2\text{O})_4]^{2+}$  unit, the metal atom is coordinated by four water molecules and two N atoms, displaying an octahedral coordination geometry. The Ni-O1, Ni-O2 and Ni-N1 distances are 0.210 9(7), 0.205 1(7) and

0.206 3 (8) nm, and the O1-Ni-O2, O1-Ni-N1 and O2-Ni-N1 bond angles are 86.8(3)°, 89.7(3)° and 90.6(3)°, respectively. In  $[\text{Ni}(\text{btec})(\text{H}_2\text{O})_4]^{2-}$  unit, four water molecules and two carboxyl oxygen atoms from two btec ions coordinate to the metal atom to complete a six-coordinated octahedral coordination geometry around Ni2 center. The O4-Ni, O5-Ni and O6-Ni distances are 0.203 7(5), 0.205 0(6) and 0.209 1(6) nm, and the O-Ni-O bond angles are in the range of 86.9(2)°~92.5(3)°. The btec ion is bound to the Ni2 center through its two para-carboxyl groups in unidentate mode. Thus, the Ni2 centers are linked up by btec ions to one-dimensional anion chain  $[\text{Ni}(\text{btec})(\text{H}_2\text{O})_4]^{2-}_n$  (Fig.2). Recently, several related Cu<sup>[12]</sup>, Co<sup>[13]</sup>, Mn<sup>[14,15]</sup>, and Ni<sup>[14,16]</sup> complexes have been reported. In these complexes, the btec ions connect the metal coordination centers through its two para-carboxyl groups to form one-dimensional anion chains  $[\text{M}(\text{btec})(\text{imi})_2(\text{H}_2\text{O})_2]^{2-}_n$  (M=Cu, Co, Mn and Ni) like that in the present complex. However, a distinct feature in the anion  $[\text{Ni}(\text{btec})(\text{H}_2\text{O})_4]^{2-}$  of the title complex is that the metal atom is coordinated by four water molecules, unlike that in the reported complexes where the metal atom is coordinated by two imidazole and two water molecules.

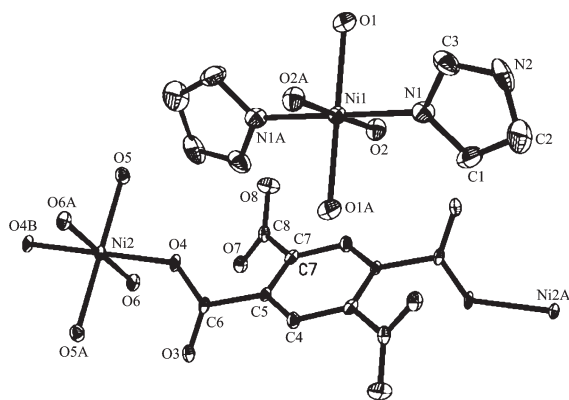


Fig.1 Locally expanded unit for the title complex with the atom numbering scheme (at 30% probability level)

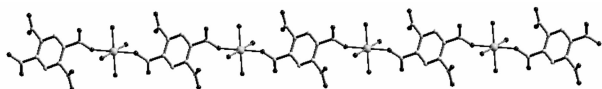
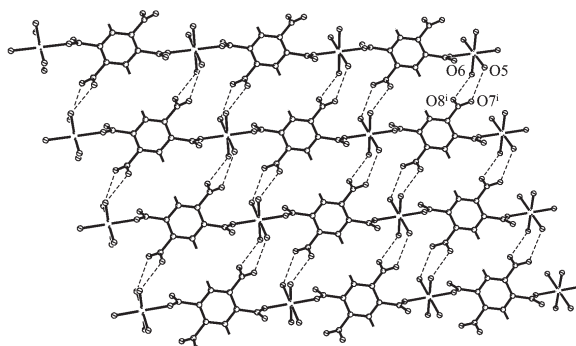


Fig.2 Chain-like structure of  $[\text{Ni}(\text{btec})(\text{H}_2\text{O})_4]^{2-}_n$

An interesting feature of the complex is that there exist hydrogen bonds between the adjacent anion

chains. The coordinated water molecules of  $[\text{Ni}(\text{btec})(\text{H}_2\text{O})_4]^{2-}$  act as hydrogen donors and the free oxygen atoms (O7 and O8) of btec ligand act as acceptors, with the O5-H...O7<sup>i</sup> and O6-H...O8<sup>i</sup> distances of 0.284 7(9) and 0.264 3(7) nm (symmetry code: <sup>i</sup>  $x, 1-y, 1-z$ ), and the corresponding O-H...O angles of 162(8)° and 177(11)°, respectively. The one-dimensional anion chains are linked up via hydrogen bonds to a two-dimensional network structure (Fig.3).



Symmetry code: <sup>i</sup>  $-x, 1-y, 1-z$

Fig.3 Two-dimensional network formed via hydrogen bonds

The IR spectrum of the title complex shows the stretching vibrations of the carboxyl group are located at 1 597  $\text{cm}^{-1}$  ( $\nu_{\text{as}}\text{COO}$ ) and 1 383  $\text{cm}^{-1}$  ( $\nu_{\text{s}}\text{COO}$ ), respectively. The  $\Delta\nu$  value ( $\nu_{\text{as}}\text{COO} - \nu_{\text{s}}\text{COO}$ ) of 214  $\text{cm}^{-1}$  suggests the unidentate coordination of the carboxyl group. Moreover, it also shows no absorptions for the protonated btec ion (1 730~1 690  $\text{cm}^{-1}$ ), indicating the complete deprotonation of btec ligand. The results are in agreement with the crystal structure as mentioned above.

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