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基于 2,4,6-吡啶三羧酸配体桥连的铁(Ⅱ)/镍(Ⅱ)配位聚合物的水热合成及结构表征

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摘要:在水热反应条件下 $FeCl_2\cdot 6H_2O$、2,4,6-吡啶三羧酸 (H_3pyta) 和 NaOH 反应合成了 1 种一维链状铁配位聚合物 $[Fe_3(pyta)_2(H_2O)_8]$ (**1**);同样条件下 $Ni(OAc)_2\cdot 4H_2O$、2,4,6-吡啶三羧酸(H_3pyta)、NaOH 和 4-氨基-3,5-二(4-吡啶基)-1,2,4-三氮唑(abpt)反应合成了 1 种二维网状镍配合物$[Ni_3(pyta)_2(abpt)_2(H_2O)_3]\cdot 2H_2O$ (**2**)。通过元素分析和红外光谱对这 2 个配位聚合物进行了表征。单晶结构表明:配合物 **1** 的晶体属于单斜晶系,*Cc* 空间群;配合物 **2** 的晶体属于单斜晶系,$P2_1/c$ 空间群。在配合物 **1** 中,$pyta^{3-}$配体采取 μ_2-和 μ_4-$pyta^{3-}$ 2 种桥连模式将 Fe 原子连成了沿 *c* 轴方向延伸的 Fe-pyta 链。而在配合物 **2** 中,$pyta^{3-}$配体仅采取 μ_2-桥连模式将 Ni 原子连成线型三核$[Ni_3(pyta)_2]$单元,这些三核单元进一步通过 abpt 辅助配体桥连成二维 (4,4)层状结构。

关键词:配位聚合物;水热反应;2,4,6-吡啶三羧酸;4-氨基-二(4-吡啶基)-1,2,4-三氮唑
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Hydrothermal Synthesis and Crystal Structure of Fe(Ⅱ)/Ni(Ⅱ) Coordination Polymers Bridged by Pyridine-2,4,6-tricarboxylate

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Abstract: Reaction of $FeCl_2\cdot 6H_2O$/$Ni(OAc)_2\cdot 4H_2O$, pyridine-2,4,6-tricarboxylic acid (H_3pyta), NaOH results in formation of a 1D Fe-pyta chain based coordination polymer $[Fe_3(pyta)_2(H_2O)_8]$ (**1**), and another 2D coordination network $[Ni_3(pyta)_2(abpt)_2(H_2O)_3]\cdot 3H_2O$ (**2**) with the auxiliary ligand 4-amino-3,5-bis(4-pyridyl)-1,2,4-triazole (abpt), both were characterized by elemental analysis and IR. X-ray diffraction crystal structure analysis shows that **1** crystallizes in monoclinic system, non-centrosymmetric space group *Cc* with *a*=1.970 2(3) nm, *b*=0.682 02(9) nm, *c*=1.948 1(2) nm, β=117.063(2)°, *V*=2.331 1(5) nm^3, *Z*=8; and **2** crystallizes in monoclinic system, space group $P2_1/c$ with *a*=1.785 19(18) nm, *b*=0.725 14(8) nm, *c*=2.072 5(2) nm, β=112.574(2)°, *V*=2.477 3(4) nm^3, *Z*=4. In complex **1**, the Fe atoms are connected by μ_2- and μ_4-$pyta^{3-}$ ligands to form a 1D Fe-pyta chain with rhombic cores along the *c*-axis. While in complex **2**, the $pyta^{3-}$ ligands adopt μ_2-bridging mode to link the Ni atoms to linear trinuclear $[Ni_3(pyta)_2]$ units, which are further connected to form 2D (4,4) coordination players by the auxiliary bridging ligand abpt. CCDC: 665831, **1**; 709969, **2**.

Key words: coordination polymer; hydrothermal reaction; pyridine-2,4,6-tricarboxylic acid; 4-amino-3,5-bis(4-pyridyl)-1,2,4-triazole

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The design and synthesis of metal-organic coordination polymers are of great interest due to their novel structural topologies examined and potential applications in host-guest chemistry, catalysis, and electrical conductivity[1~3]. In the rational design and synthesis of metal-organic coordination compounds, several factors are always taken into considerations, such as the coordination nature of metal ions, the functionality, flexibility and symmetry of organic ligands, and the template effect of structure-directing agents[4~6]. 3- and 4-pyridinecarboxylate and pyridinedicarboxylate have recently been found to act as excellent building blocks with charge and multi-connecting ability in the construction of functional coordination polymers with porosity, photoluminescent or magnetic properties [7,8]. Compared with the previously investigated pyridinecarboxylate ligands, pyridine-2,4,6-tricarboxylic acid (H_3pyta) have the advantages of multiple bridging moieties, which leads to a variety of connection modes with transition metal centers and provides abundant structural motifs. It can act not only as *N*-donors but also as $O_{carboxylate}$-donors to chelate or bridge metal ions to coordination polymers[9,10]. In our recent work, pyridine-2,4,6-tricarboxylic acid (H_3pyta) with 3d-4f metal ions have been used to construct coordination polymers with magnetic property or adsorption behavior[11,12]. In this contribution, H_3pyta was employed to synthesize a 1D Fe-pyta chain based coordination polymers $[Fe_3(pyta)_2(H_2O)_8]$ (**1**).

As is well known, the 4-amino-3,5-bis(4-pyridyl)-1,2,4-triazole (abpt) can be a good *N*,*N*′-donor building block that have been studied in coordination chemistry[13~15]. As our continuous study of pyridine-2,4,6-tricarboxylate coordination polymers[16,17], in this contribution, H_3pyta was employed to synthesize a new 1D Fe-pyta chains based coordination polymer $[Fe_3(pyta)_2(H_2O)_8]$ (**1**); and another 2D coordination network $[Ni_3(pyta)_2(abpt)_2(H_2O)_3]\cdot 3H_2O$ (**2**) constructed by $[Ni_3(pyta)_2]$ units and the bridging 4-amino-3,5-bis(4-pyridyl)-1,2,4-triazole (abpt) ligands.

1 Experimental Section

1.1 Materials and physical measurements

The $FeCl_2\cdot 6H_2O$ and $Ni(OAc)_2\cdot 4H_2O$ were commercially available and used as received without further purification. Pyridine-2,4,6-tricarboxylic acid (H_3pyta) was synthesized according to their literature methods[18]. 4-amino-3,5-bis (4-pyridyl)-1,2,4-triazole (abpt) ligand could be obtained directly from the two reactants by employing the one-pot procedure described by Lagrenée and co-workers[19]. The C, H and N microanalyses were carried out with an Elementar Vario-EL CHN elemental analyzer. The IR spectra were recorded from KBr tablets in the range 4 000~400 cm^{-1} on a Bio-Rad FTS-7 spectrometer.

1.2 Hydrothermal synthesis

$[Fe_3(pyta)_2(H_2O)_8]$ (**1**), A mixture of $FeCl_2\cdot 6H_2O$ (352 mg, 1.5 mmol), H_3pyta (211 mg, 1 mmol), NaOH (120 mg, 3 mmol) and H_2O (10 mL) was sealed in a 23 mL Teflon-lined reactor and heated in an oven at 185 ℃ for 72 hrs and then at 90 ℃ for 12 hrs. After 15 hrs′ gradual cooling to room temperature, black-red crystals of 1 (yield 51% based on H_3pyta) were obtained, and then filtered, washed, and dried in air. Anal. Calcd. for $C_{16}H_{20}Fe_3N_2O_{20}$ (%): C, 26.40; H, 2.77; N, 3.85. Found (%): C, 26.29; H, 2.82; N, 3.92. IR (KBr, cm^{-1}): 3 420 (s), 1 577(vs), 1 408(m), 1 019(w), 923(w), 650(m).

$[Ni_3(pyta)_2(abpt)_2(H_2O)_3]\cdot 2H_2O$ (**2**), A mixture of $Ni(OAc)_2\cdot 4H_2O$ (249 mg, 1 mmol), abpt (117 mg, 0.5 mmol), H_3pyta (106 mg, 0.5 mmol), NaOH (20 mg,0.5 mmol) and H_2O (10 mL) was sealed in a 23 mL Teflon-lined reactor and heated in an oven at 185 ℃ for 72 hrs and then at 90 ℃ for 12 hrs period. After 15 hrs′ gradual cooling to room temperature, green crystals of 2 (yield 64% based on H_3pyta) were obtained, and then filtered, washed, and dried in air. Anal. Calcd. for $C_{40}H_{48}N_{14}Ni_3O_{24}$ (%): C, 37.39; H, 3.77; N, 15.26. Found (%): C, 37.47; H, 3.82; N, 15.15. IR (KBr, cm^{-1}): 3 653 (w), 3 358 (s), 1 634 (s), 1 562 (m), 1 474 (w), 1 436(m), 1 365(s), 1 316(m), 1 276(m), 1 217(w), 1 086(vw), 990 (vw), 931(vw), 842(m), 785(m), 743(s), 619(w), 540(w).

1.3 Crystal structure determination

Data collection of **1** and **2** was performed on a Bruker Smart Apex 1000 CCD diffractometer with Mo $K\alpha$ radiation (λ=0.071 073 nm) at 293(2) K. The raw data frames were integrated with SAINT$^+$, and the corrections were applied for Lorentz and polarization

effects. Absorption correction was applied by using the program SADABS[20]. The structures were solved by direct methods, and all non-hydrogen atoms were refined anisotropically by least-squares on F^2 using the SHELXTL program[21]. Hydrogen atoms on organic ligands were generated by the riding mode (C-H=0.093 nm). Crystal data as well as details of data collection and refinements for complexes **1** and **2** are summarized in Table 1. Selected bond distances and bond angles are listed in Table 2.

CCDC: 665831, **1**; 709969, **2**.

Table 1　Crystal data and structure parameters for complexes 1 and 2

Identification code	**1**	**2**
Empirical formula	$C_{16}H_{20}Fe_3N_2O_{20}$	$C_{40}H_{48}N_{14}Ni_3O_{24}$
Formula weight	727.89	1 285.05
Temperature / K	293(2)	293(2)
Wavelength	0.710 73	0.710 73
Crystal system	Monoclinic	Monoclinic
Space group	*Cc*	$P2_1/c$
a / nm	1.970 2(3)	1.785 19(18)
b / nm	0.682 02(9)	0.725 14(8)
c / nm	1.948 1(2)	2.072 5(2)
β / (°)	117.063(2)	112.574(2)
Volume / nm^3	2.331 1(5)	2.477 3(4)
Z	4	2
D_c / ($g\cdot cm^{-3}$)	2.074	1.723
Absorption coefficient / mm^{-1}	1.949	1.232
F(000)	1 472	1 324
Crystal size / mm	0.26×0.21×0.19	0.16×0.10×0.08
θ range for data collection / (°)	2.35~26.00	3.01~26.00
Limiting indices	$-24 \leqslant h \leqslant 24, -8 \leqslant k \leqslant 8, -23 \leqslant l \leqslant 17$	$-20 \leqslant h \leqslant 20, -8 \leqslant k \leqslant 5, -22 \leqslant l \leqslant 25$
Reflections collected	5 665	9 424
Independent reflections (R_{int})	3 420 (0.044 9)	4 693 (0.042 6)
Observed reflections [$I>2\sigma(I)$]	3 235	3 354
Completeness / %	99.5	96.6
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3 420 / 12 / 370	4 693 / 20 / 415
Goodness-of-it on F^2	1.013	0.911
Final R indices [$I>2\sigma(I)$] R_1[a], wR_2[b]	0.040 3, 0.096 7	0.042 2, 0.086 0
R indices (all data) R_1[a], wR_2[b]	0.042 1, 0.097 9	0.060 2, 0.091 5
Largest diff. peak and hole	1.559, −0.658	0.609, −0.321

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

Table 2　Bond lengths (nm) and angles (°) for 1 and 2

1					
Fe(1)-O(8a)	0.209 0(4)	Fe(2)-O(4a)	0.207 5(4)	Fe(3)-O(5)	0.206 0(4)
Fe(1)-N(1)	0.210 3(4)	Fe(2)-O(5W)	0.210 0(4)	Fe(3)-O(7W)	0.210 1(5)
Fe(1)-O(1W)	0.212 3(4)	Fe(2)-O(4W)	0.212 1(4)	Fe(3)-N(2)	0.214 3(5)
Fe(1)-O(2W)	0.214 3(4)	Fe(2)-O(6W)	0.213 4(4)	Fe(3)-O(8W)	0.217 8(4)
Fe(1)-O(1)	0.216 6(4)	Fe(2)-O(2)	0.213 9(4)	Fe(3)-O(12)	0.219 6(4)
Fe(1)-O(6)	0.222 5(5)	Fe(2)-O(3W)	0.216 9(5)	Fe(3)-O(7)	0.222 3(6)

Continued Table 2

O(8a)-Fe(1)-N(1)	157.4(2)	O(4a)-Fe(2)-O(5W)	85.11(18)	O(5)-Fe(3)-O(7W)	81.20(17)
O(8a)-Fe(1)-O(1W)	83.65(17)	O(4a)-Fe(2)-O(4W)	104.01(16)	O(5)-Fe(3)-N(2)	171.57(18)
N(1)-Fe(1)-O(1W)	98.53(17)	O(5W)-Fe(2)-O(4W)	90.05(18)	O(7W)-Fe(3)-N(2)	100.57(18)
O(8a)-Fe(1)-O(2W)	87.29(17)	O(4a)-Fe(2)-O(6W)	86.41(18)	O(5)-Fe(3)-O(8W)	86.69(16)
N(1)-Fe(1)-O(2W)	91.90(16)	O(5W)-Fe(2)-O(6W)	99.54(18)	O(7W)-Fe(3)-O(8W)	167.83(18)
O(1W)-Fe(1)-O(2W)	169.46(16)	O(4W)-Fe(2)-O(6W)	166.48(18)	N(2)-Fe(3)-O(8W)	91.24(17)
O(8a)-Fe(1)-O(1)	128.4(2)	O(4a)-Fe(2)-O(2)	163.21(15)	O(5)-Fe(3)-O(12)	99.03(16)
N(1)-Fe(1)-O(1)	74.19(16)	O(5W)-Fe(2)-O(2)	86.37(16)	O(7W)-Fe(3)-O(12)	97.2(2)
O(1W)-Fe(1)-O(1)	89.65(17)	O(4W)-Fe(2)-O(2)	90.43(15)	N(2)-Fe(3)-O(12)	72.60(17)
O(2W)-Fe(1)-O(1)	91.80(17)	O(6W)-Fe(2)-O(2)	80.77(17)	O(8W)-Fe(3)-O(12)	83.41(17)
O(8a)-Fe(1)-O(6)	84.7(2)	O(4a)-Fe(2)-O(3W)	95.13(18)	O(5)-Fe(3)-O(7)	116.65(18)
N(1)-Fe(1)-O(6)	72.63(17)	O(5W)-Fe(2)-O(3W)	174.84(19)	O(7W)-Fe(3)-O(7)	82.9(2)
O(1W)-Fe(1)-O(6)	96.19(18)	O(4W)-Fe(2)-O(3W)	84.89(18)	N(2)-Fe(3)-O(7)	71.78(19)
O(2W)-Fe(1)-O(6)	88.28(17)	O(6W)-Fe(2)-O(3W)	85.61(19)	O(8W)-Fe(3)-O(7)	103.86(19)
O(1)-Fe(1)-O(6)	146.81(15)	O(2)-Fe(2)-O(3W)	94.66(17)	O(12)-Fe(3)-O(7)	143.75(19)
		2			
Ni(1)-N(1)	0.197 4(2)	Ni(1)-O(2W)	0.207 7(3)	Ni(2)-O(1Wb)	0.208 7(2)
Ni(1)-N(7a)	0.204 3(3)	Ni(1)-O(2)	0.214 9(2)	Ni(2)-O(1W)	0.208 7(2)
Ni(1)-O(3W)	0.206 5(3)	Ni(2)-O(6b)	0.206 4(2)	Ni(2)-N(6b)	0.209 3(3)
Ni(1)-O(5)	0.207 7(2)	Ni(2)-O(6)	0.206 4(2)	Ni(2)-N(6)	0.209 3(3)
N(1)-Ni(1)-N(7a)	176.60(11)	N(1)-Ni(1)-O(2)	77.42(10)	O(1Wb)-Ni(2)-O(1W)	180.0
N(1)-Ni(1)-O(3W)	95.21(11)	N(7a)-Ni(1)-O(2)	105.23(10)	O(6b)-Ni(2)-N(6b)	85.91(9)
N(7a)-Ni(1)-O(3W)	86.75(11)	O(3W)-Ni(1)-O(2)	94.42(12)	O(6)-Ni(2)-N(6b)	94.09(9)
N(1)-Ni(1)-O(5)	78.75(9)	O(5)-Ni(1)-O(2)	156.12(8)	O(1Wb)-Ni(2)-N(6b)	89.43(10)
N(7a)-Ni(1)-O(5)	98.64(10)	O(2W)-Ni(1)-O(2)	85.98(11)	O(1W)-Ni(2)-N(6b)	90.57(10)
O(3W)-Ni(1)-O(5)	86.30(11)	O(6b)-Ni(2)-O(6)	180.00(13)	O(6b)-Ni(2)-N(6)	94.09(9)
N(1)-Ni(1)-O(2W)	89.41(12)	O(6b)-Ni(2)-O(1Wb)	87.70(10)	O(6)-Ni(2)-N(6)	85.91(9)
N(7a)-Ni(1)-O(2W)	88.66(12)	O(6)-Ni(2)-O(1Wb)	92.30(10)	O(1Wb)-Ni(2)-N(6)	90.57(10)
O(3W)-Ni(1)-O(2W)	175.34(12)	O(6b)-Ni(2)-O(1W)	92.30(10)	O(1W)-Ni(2)-N(6)	89.43(10)
O(5)-Ni(1)-O(2W)	95.21(11)	O(6)-Ni(2)-O(1W)	87.70(10)	N(6b)-Ni(2)-N(6)	180.0

Symmetry codes for **1**: (a) $x+1/2, -y+1/2, z+1/2$; (b) $x-1/2, -y+1/2, z-1/2$; for 2: (a) $x-1, -y-5/2, z-1/2$; (b) $-x-1, -y-3, -z$.

2 Results and discussion

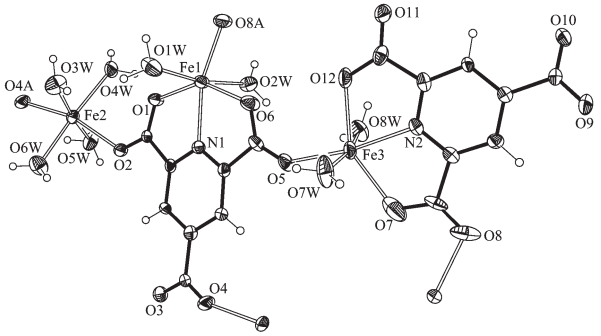
2.1 Synthesis

As is well known, there are a variety of hydrothermal parameters such as time, temperature, pH value, and molar ratio of reactants, and small changes in one or more of the parameters can have a profound influence on the final reaction outcome[22]. In our previous work, we have reported a 1D Fe-pyta chain based coordination polymers $[Fe(Hpyta)(H_2O)_2]$[16], obtained by the reaction of $FeCl_2 \cdot 6H_2O$, H_3pyta and NaOH in the molar ratio of 1∶1∶3 in the hydrothermal system at 185 ℃. Considering the various connection modes of pyta ligand, we increased the molar ratio to 1.5∶1∶3, resulting the complex **1** based on Fe-pyta ladder-like chains with both μ_4-pyta and μ_2-pyta bridging ligands. Differently, there was no crystals obtained when the similar reaction reacted with Ni(Ⅱ) ions. However, when the auxiliary ligand abpt was employed into the reaction system, complex **2** was

obtained, which was a 2D coordination polymer constructed by $[Ni_3(pyta)_2]$ units and the bridging abpt, compared to the $(H_2bpt)[Fe(pyta)(H_2O)_2]\cdot 4H_2O$ (H_2bpt= protonated 3,5-bis(4-pyridyl)-4H-1,2,4-triazol)[14].

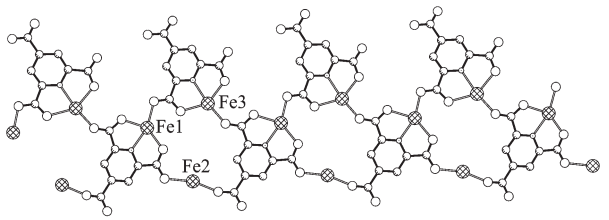
2.2 Structure of $[Fe_3(pyta)_2(H_2O)_8]$ (1)

Single crystal structure shows that complex **1** crystallizes in the monoclinic non-centrosymmetric space group *Cc*, with containing three crystallographically unique Fe(Ⅱ) atoms, two deprotonated $pyta^{3-}$ ligand and eight coordinated water molecules, all of which are on general positions (Fig.1). All of the three Fe(Ⅱ) atoms adopt greatly distorted octahedral coordination geometry: Fe1 and Fe3 are similarly coordinated to three O atoms and one N atom from the $pyta^{3-}$ ligand and two water molecules (Fe1-O=0.209 1(5)~0.222 4(5) nm; Fe1-N=0.210 3(4) nm; O-Fe1-O=83.62(17)°~169.39(17)°; O-Fe1-N=72.63(17)°~157.4(2)°) (Fe3-O=0.206 0(5)~0.222 5(7) nm; Fe3-N=0.214 3(5) nm; O-Fe3-O=81.15(19)°~167.8(2)°; O-Fe3-N=71.8(2)°~171.54(18)°), while Fe2 is coordinated to two O atoms from the $pyta^{3-}$ ligand and four water molecules (Fe2-O=0.207 5(4)~0.214 0(4) nm; O-Fe2-O=85.17(19)°~166.5(2)°). There are two coordination modes of the $pyta^{3-}$ ligand, one of which adopts μ_4-bridged mode connecting to four metal atoms and the other adopts μ_2-bridged mode (Scheme 1). Interestingly, three metal atoms and three $pyta^{3-}$ ligand (two μ_4-bridged and one μ_2-bridged) form a distorted rhombic core, each of which is stringed by the shared μ_4-bridged $pyta^{3-}$ ligand into the Fe-pyta chain along the c-axis (Fig.2). These cores are filled with the coordinated water molecules. Adjacent chains are packed in offset face-to-face AB method (Fig.3) through π-π interactions between the two pyridyl planes with the distance of 0.36 nm and rich hydrogen-bonds (O⋯O=0.272 2~0.289 2 nm, O-



A: x+1/2, −y+1/2, z+1/2; B: x−1/2, −y+1/2, z−1/2

Fig.1 Coordination environment of Fe(Ⅱ) atoms and coordination modes of pyta ligand in a asymmetric unit of **1**



Water molecules are omitted for clarity

Fig.2 Perspective view of the Fe-pyta ladder-like chain along the *c*-axis of **1**

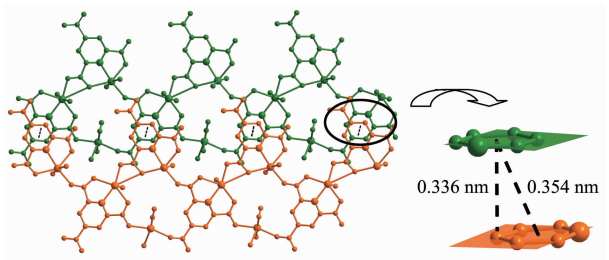
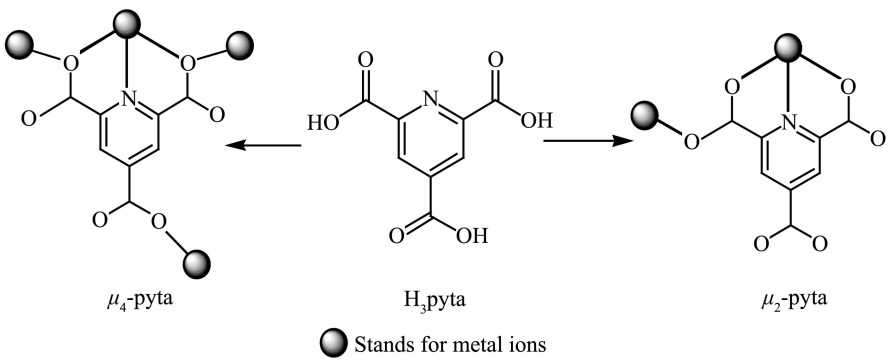


Fig.3 Perspective view of the Fe-pyta chains packed in offset face-to-face AB method through π-π interactions (the distances of the two pyridyl planes 0.336 nm and the two centers 0.354 nm) of **1**



Scheme 1 Coordination modes of pyta in complex **1** and **2**

HO =150.39° ~167.29°) (Fig.4) between the water molecules and the carboxylate groups to generate a 3D supramolecular structure.

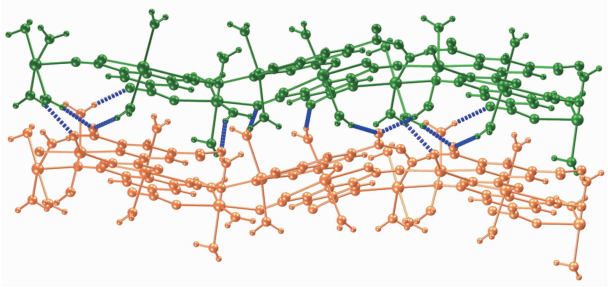
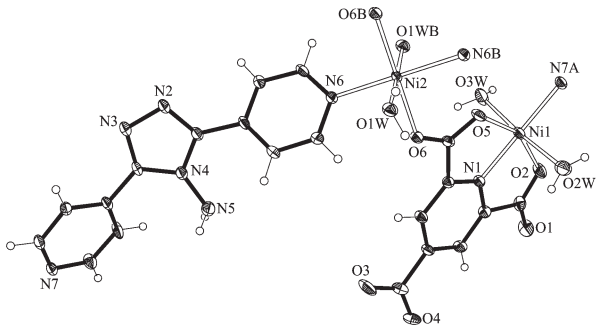


Fig.4 Perspective view of the hydrogen-bonds between the water molecules and the carboxylate groups of the adjacent packed Fe-pyta chains of **1**

2.3 Structure of $[Ni_3(pyta)_2(abpt)_2(H_2O)_3]\cdot 3H_2O$ (2)

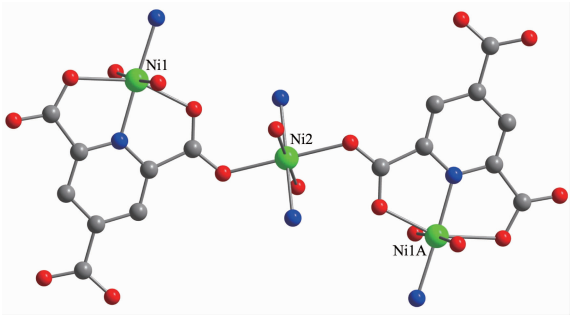
The crystal structure reveals that complex **2** is a 2D coordination polymer based on trinuclear $[Ni_3(pyta)_2]$ units by the bridging abpt ligands. There are two uniqe Ni(Ⅱ) atoms, one of which lies on special position, one deprotonated $pyta^{3-}$ ligand, three coordinated and three lattice water molecules in the asymmetric unit (Fig.5). Ni1 has six-coordinate octahedral coordination environment with two O atoms and two N atom from the carboxylate group and pyridyl ring of the $pyta^{3-}$ ligands and abpt ligand (Ni1-O=0.207 7(2) and 0.214 9(2) nm; Ni1-N=0.197 4(2) and 0.204 3(3) nm; O-Ni1-O=156.12(8)°; O-Ni1-N=77.42(10)°~105.23(10)°; N-Ni1-N=176.60(11)°) at basal positions and two water molecules at the apical positions (Ni1-O1W=0.206 5(3) and 0.207 7(3) nm; O1W-Ni1-O1W=175.34(12)°; O1W-Ni1-N/O=86.75(11)° ~94.42(12)°). Ni2 atom, which lies on special position, also adopts hexagonal octahedral coordination geometry with two O atoms and two N atom from the carboxylate group and pyridyl ring of the $pyta^{3-}$ ligands (Ni2-O= 0.207 7(2) and 0.214 9(2) nm; Ni2-N=0.197 4(2) and 0.204 3(3) nm; O-Ni2-O=156.12(8)°; O-Ni2-N=77.42(10)° ~105.23(10)°; N-Ni2-N=176.60(11)°) at basal positions and two water molecules at the apical positions (Ni2-O1W=0.206 5(3) and 0.207 7(3) nm; O1W-Ni2-O1W= 175.34(12)°; O1W-Ni2-N/O=86.75(11)° ~94.42(12)°). The $pyta^{3-}$ ligand connects two Ni atoms to form a μ_2-bridging mode (Scheme 1).



A: $x-1, -y-5/2, z-1/2$; B: $-x-1, -y-3, -z$

Fig.5 Coordination environment of Ni atoms in the asymmetric unit of **2**

Interestingly, three Ni(Ⅱ) atoms containing two Ni1 and one Ni2 form a linear trinuclear $[Ni_3(pyta)_2]$ unit bridged by μ_2-pyta ligand (Fig.6), which is different from the Fe-pyta chain in complex **1**. Furthermore, the bridging abpt ligands link the $[Ni_3(pyta)_2]$ units (Fig.7a) to generate a 2D (4,4) layer (Fig.7b), in which the $[Ni_3(pyta)_2]$ units act as the 4-connected nodes and abpt as the spacers. The lattice water molecules are located



A: $-1-x, -3-y, -z$

Fig.6 Linear trinuclear units $[Ni_3(pyta)_2]$ bridged by $pyta^{3-}$ ligand in **2**

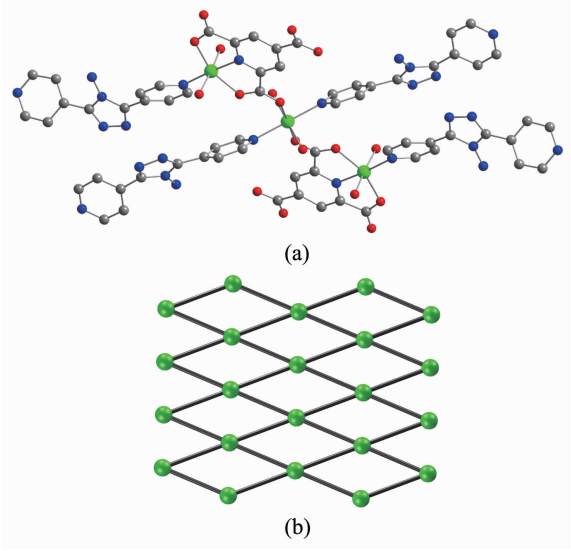


Fig.7 4-connected $[Ni_3(pyta)_2]$ node (a) and (4,4) topological coordination layer (b) in **2**

in the space between two layers with rich hydrogen bonds (O⋯O=0.267 9(4)~0.299 2(6) nm, O–H⋯O= 154(3)°~175(4)°). The 2D layers are linked to a 3D supramolecular through weak π-π interactions and hydrogen-bonds (Fig.8).

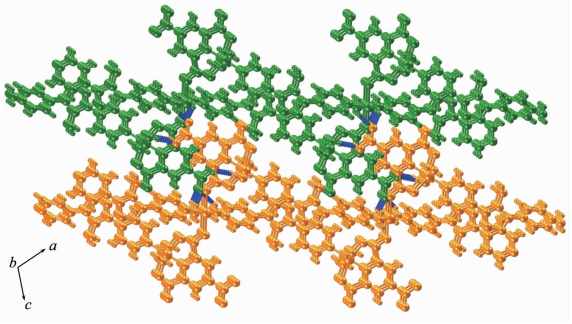


Fig.8 Perspective view of the 2D coordination layer packed to 3D supramolecular network through weak π-π interactions and hydrogen-bonds in 2

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