

1,10-邻菲咯啉和四氟对苯二甲酸构建的两个镍(II)的配合物:合成和晶体结构

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摘要: 以醋酸镍、四氟对苯二甲酸(H₂tfbdc)及 1,10-邻菲咯啉(phen)为原料在不同的反应条件下合成了 2 个镍(II)的配合物[[Ni(phen)₂(Htfbdc)]₂(μ-tfbdc)]·3H₂O (**1**·3H₂O)和[Ni(phen)₃]₂(tfbdc)₂·13H₂O (**2**·13H₂O)。单晶结构分析显示配合物 **1**·3H₂O 中 3D 超分子结构在 C-H...O/F 和 C-F...π 弱相互作用下而成;在配合物 **2**·13H₂O 中,水分子和羧酸离子构建的三维氢键框架中含有金属有机离子链客体。此外,在这些 3D 超分子结构中强氢键作用、C-H...O 和 C-H...F 等弱氢键作用,π...π 及 C-F/H...π 作用均起到了稳定结构的作用。

关键词: 镍; 四氟对苯二甲酸; 氢键; 反应条件; 晶体结构

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Two Nickel(II) Complexes with 1,10-Phenanthroline and Tetrafluoroterephthalic Acid: Synthesis and Structures

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Abstract: Treatment of Ni(OAc)₂·4H₂O with tetrafluoroterephthalic acid (H₂tfbdc) and 1,10-phenanthroline (phen) in different reaction conditions afforded {[Ni(phen)₂(Htfbdc)]₂(μ-tfbdc)}·3H₂O (**1**·3H₂O) and [Ni(phen)₃]₂(tfbdc)₂·13H₂O (**2**·13H₂O). Single crystal analysis shows that there is a 3D supramolecular structure constructed by C-H...O/F and C-F...π weak interactions in **1**·3H₂O and an interesting 3D hydrogen-bonded water-carboxylate anions framework acting as “host” to encapsulate the 1D metal-organic cationic “guest” in **2**·13H₂O. Besides the strong hydrogen bond interactions, weak hydrogen bonds (e.g., C-H...O and C-H...F), π...π stacking and C-F/H...π interactions also play role in contributing to the stability of these 3D supramolecular architectures. CCDC: 830629, **1**·3H₂O; 830630, **2**·13H₂O.

Key words: nickel; tetrafluoroterephthalate; hydrogen bond; reaction condition; crystal structure

0 Introduction

In the past decades, considerable attention has

been focused on the supramolecular hybrid materials assembled by covalent bonds and the non-covalent forces, including hydrogen bonds and π...π interac-

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tions^[1-5], owing to their intriguing structural features and potential applications in catalysis, separation, gas storage, optoelectronics, and so forth^[6-11]. It is well-known that the reaction conditions play important roles in the design and syntheses of desirable complexes, the changes in the reaction conditions such as the synthetic route, the reaction temperature, pH value, and the metal-to-ligand ratio, can result in a remarkable class of materials bearing diverse architectures and functions^[12-14]. There have been several recent reports, in which the effect of synthetic method on the self-assembly of metal ions and ligands have been used to construct coordination polymers showing novel structural features^[15]. For example, Du et al have reported a series of Zn (II) or Cd (II) coordination polymers containing 5-(4-pyridyl)-1,3,4-oxadiazole-2-thiol, generated through control of the synthetic routes with the same reactants, which display diverse coordination networks from one-dimension (1D), two-dimension (2D), to three-dimension (3D)^[16]. However, studies on the influences of the reaction conditions on the formation of supramolecular networks constructed by the second interactions such as hydrogen bonds, $\pi \cdots \pi$ stacking and C-F/H $\cdots \pi$ interactions are less explored. Therefore, we deliberately chose Ni(OAc)₂·4H₂O to react with tetrafluoroterephthalic acid (H₂tfbdc) and 1,10-phenanthroline (phen) in aqueous methanol solutions via two different synthetic routes: one is routine solution reaction, the other is solvothermal reaction, and isolated two complexes {[Ni(phen)₂(Htfbdc)]₂(μ -tfbdc)}·3H₂O (**1**·3H₂O) and [Ni(phen)₃]₂(tfbdc)₂·13H₂O (**2**·13H₂O). X-ray diffraction analyses reveal that **2**·13H₂O and **1**·3H₂O contain mono- and dinuclear Ni^{II} components respectively, which serve as building blocks to further expand to two 3D inorganic-organic supramolecular assemblies through the second interactions such as hydrogen bonds (e.g., O-H \cdots O, C-H \cdots O and C-H \cdots F), $\pi \cdots \pi$ stacking and C-F/H $\cdots \pi$ interactions. The results represent an example in which the same reactants produced two different supramolecular assemblies through two different synthetic routes. Herein we report the synthesis and crystal structure of the complexes **1**·3H₂O and **2**·13H₂O.

1 Experimental

1.1 Materials and methods

All reagents and solvents for synthesis and analysis were commercially available and used as received. Infrared spectra were recorded with a Nicolet ESP 460 FT-IR spectrometer on KBr pellets in the range of 4 000~600 cm⁻¹. Carbon, hydrogen, and nitrogen analyses were performed on a PE-2400II (Perkin-Elmer) analyzer. Single-crystal X-ray diffraction measurement of the title compounds were carried out with a Bruker Apex II CCD diffractometer at 292(2) K. Powder X-ray diffraction (PXRD) determinations were performed on an X-ray diffractometer (D/max 2500 PC, Rigaku) with Cu K α radiation (0.154 06 nm).

1.2 Synthesis

1.2.1 Preparation of {[Ni(phen)₂(Htfbdc)]₂(μ -tfbdc)}·3H₂O (**1**·3H₂O)

To a 2 mL aqueous solution of Ni(OAc)₂·4H₂O (0.024 9 g, 0.1 mmol), a solution of H₂tfbdc (0.047 6 g, 0.2 mmol) and phen·H₂O (0.039 6 g, 0.2 mmol) in 4 mL methanol was added and stirred for 1 h. Slow evaporation of the solvents from the resulting purple solution produced blue blocks of {[Ni(phen)₂(Htfbdc)]₂(μ -tfbdc)}·3H₂O (**1**·3H₂O), which were collected by filtration, washed thoroughly with Et₂O and dried in air (Yield 0.057 g, 71%, based on Ni). Analysis found (%): C 53.85, H 2.43, N 6.97; Calcd. for C₇₂H₄₀Ni₂F₁₂N₈O₁₅ (%): C 53.96, H 2.52, N 6.99. IR (KBr, cm⁻¹): 3 423 (s), 3 075(s), 2 561(m), 1 972(w), 1 720(m), 1 642(vs), 1 587(s), 1 518(m), 1 496(m), 1 471(s), 1 426(s), 1 366 (vs), 1 341(s), 1 304(s), 1 226(m), 1 146(m), 1 106(m), 1 051(w), 989(s), 978(m), 887(w), 856(s), 843(s), 789 (w), 738(s), 730(vs), 708(m), 643(s), 508(w), 462(w), 426(m).

1.2.2 Preparation of [Ni(phen)₃]₂(tfbdc)₂·13H₂O (**2**·13H₂O)

A mixture of Ni(OAc)₂·4H₂O (0.024 9 g, 0.1 mmol), H₂tfbdc (0.047 6 g, 0.2 mmol), phen·H₂O (0.039 6 g, 0.2 mmol), 4 mL methanol and 2 mL H₂O was stirred for 1 h and then placed in a sealed Teflon-lined stainless steel vessel, heated at 100 °C for 2 d and allowed to cool to room temperature over 24 h. The

resulting purple solution was filtrated, then the filtrate was slowly evaporated (1 week), blue needle crystals of $[\text{Ni}(\text{phen})_3]_2(\text{tfbdc})_2 \cdot 13\text{H}_2\text{O}$ (**2**·13H₂O) were obtained in 43% yield (0.027 g, based on phen·H₂O). Analysis found (%): C 55.74, H 4.25, N 8.37; Calcd. for C₈₈H₇₄F₈N₁₂Ni₂O₂₁(%): C 55.48, H 3.92, N 8.82. IR (KBr, cm⁻¹): 3 519(s), 3 222(s), 3 031(s), 1 930(w), 1 822(w), 1 631(vs), 1 601(s), 1 519(s), 1 496(vs), 1 429(s), 1 363(s), 1 234(m), 1 168(s), 1 145(m), 1 105(m), 984(m), 946(vs), 896(w), 848(s), 769(m), 747(s), 727(vs), 706(s), 644(s), 527(w), 505(m), 425(w), 413(m).

1.3 X-ray crystallography

X-ray single crystal diffraction data for crystals **1**·3H₂O and **2**·13H₂O were collected on a Bruker Smart Apex CCD diffractometer at 292(2) K with Mo K α

radiation ($\lambda=0.071\ 073\ \text{nm}$) by ω scan mode. Both structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL^[17]. The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for all the non-hydrogen atoms on F^2 . H atoms attached to C were placed geometrically and allowed to ride during subsequent refinement with an isotropic displacement parameter fixed at 1.2 times Ueq of the parent atoms. H atoms bonded to O or N were located in difference Fourier maps. The O(3) atom of the uncoordinated carboxyl group in the structure **1**·3H₂O was found to be disordered over two positions with an occupancy ratio of 0.66/0.34 for O(3)/O(3A). Ten water (O(9)~O(18)) molecules in **2**·13H₂O

Table 1 Crystal structure data for **1**·3H₂O and **2**·13H₂O

	1 ·3H ₂ O	2 ·13H ₂ O
Formula	C ₇₂ H ₄₀ F ₁₂ N ₈ Ni ₂ O ₁₅	C ₈₈ H ₇₄ F ₈ N ₁₂ Ni ₂ O ₂₁
Formula weight	1 602.54	1 905.01
Crystal size / nm	0.30×0.20×0.15	0.20×0.15×0.10
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	Cc
a / nm	0.897 6(6)	2.161 8(9)
b / nm	1.015 1(6)	1.808 8(8)
c / nm	1.815 7(11)	2.500 9(10)
α / (°)	91.619(8)	
β / (°)	92.542(7)	112.456(5)
γ / (°)	95.733(7)	
V / nm ³	1.643 6(18)	9.038(6)
Z	1	4
D_c / (g·cm ⁻³)	1.619	1.4
$\mu(\text{Mo } K\alpha)$ / cm ⁻¹	6.85	5.1
$F(000)$	812	3 928
hkl range	$-10 \leq h \leq +10, -11 \leq k \leq +12, -21 \leq l \leq +21$	$-26 \leq h \leq +26, -22 \leq k \leq +22, -25 \leq l \leq +30$
$((\sin\theta)/\lambda)_{\text{max}}$ / nm ⁻¹	0.451	0.489
Refl. measured	11 435	35 060
Refl. unique	5 668	15 464
Observed refl	4 829	13 244
R_{int}	0.030 0	0.042 6
Param. refined	501	1 225
$R(F)/wR(F^2)^a$ (all reflexions)	0.097 2 / 0.277 5	0.063 9 / 0.143 4
$\chi(\text{Flack})$		0.01 6(10)
GoF (F^2) ^a	1.124	1.062
$(\Delta\rho)_{\text{max}} (\Delta\rho)_{\text{min}}$ / (e·nm ⁻³)	1 185, -788	248, -532

^a Definition of R values and GoF, as well as information on weighting scheme applied

were fixed with constrained parameters and refined with an occupancy factor of 0.5. Further details for crystallographic data and structural analysis are listed in Table 1.

CCDC: 830629, **1**·3H₂O; 830630, **2**·13H₂O.

2 Results and discussion

2.1 Synthesis

1·3H₂O and **2**·13H₂O were obtained by the same reactants Ni(OAc)₂·4H₂O, H₂tfbdc and phen, in the same molar ratio of 1:1:2 in aqueous methanol solutions, via two different synthetic routes: routine solution reaction and solvothermal reaction, respectively. The difference between the structures of **1**·3H₂O and **2**·13H₂O implies that the reaction temperature and pressure did affect the structures of complexes. Compounds **1**·3H₂O and **2**·13H₂O were relatively air- and moisture-stable, insoluble in water or most organic solvents, being consistent with their neutral nature. The elemental analyses of **1**·3H₂O and **2**·13H₂O were consistent with their chemical formulae.

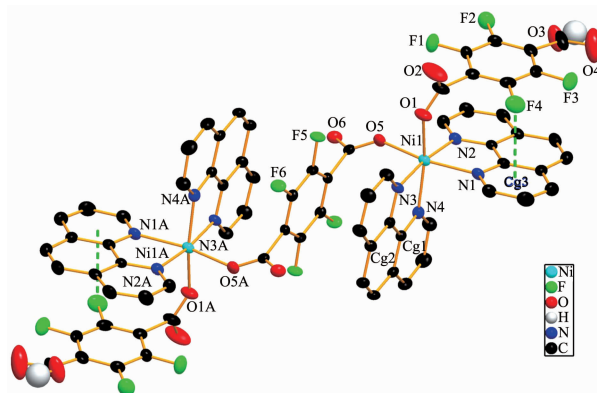
2.2 IR spectra

The IR spectra of **1** and **2** are featured by the absorption bands arising from tfbdc²⁻/Htfbdc⁻ and phen ligands. The peaks at 1 640~1 580 cm⁻¹ and 1 460~1 400 cm⁻¹ are the asymmetric stretching vibration $\nu_{as}(\text{COO}^-)$ and the symmetric stretching vibration $\nu_s(\text{COO}^-)$ of tfbdc²⁻, respectively. In the IR spectrum of **2**, the absence of absorption bands at 1 690~1 730 cm⁻¹ could be designated to the complete deprotonation of H₂tfbdc upon its reaction with Ni^{II} ions. The peaks at 1 518 (**1**) and 1 519 cm⁻¹ (**2**) is characteristic $\nu_{as}(\text{C}=\text{N})$ of the coordinated phen. The identities of **1**·3H₂O and **2**·13H₂O were finally confirmed by X-ray crystallography.

2.3 Structure description for {[Ni(phen)₂(Htfbdc)]₂(μ -tfbdc)}·3H₂O (**1**·3H₂O)

Complex **1**·3H₂O crystallizes in the triclinic space group $P\bar{1}$ and the asymmetric unit contains one-half of the dimeric molecule {[Ni(phen)₂(Htfbdc)]₂(μ -tfbdc)} and one and a half of solvent water molecules. As shown in Fig.1, complex **1** consists of two [Ni(phen)₂(Htfbdc)]⁺ moieties interconnected by a bis-monodentate μ -tfbdc²⁻

anion, forming a dimeric structure with a crystallographic center of symmetry at the midpoint of Ni(1) and Ni(1A) atoms. Two types of coordination modes for anions of H₂tfbdc ligands are present in the structure: (a) each carboxylate group of tfbdc²⁻ anion adopts a monodentate mode, bridging two Ni^{II} ions; (b) H₂tfbdc ligand is partially deprotonated, forming Htfbdc⁻ anion, which coordinates with Ni^{II} ions in monodentate mode. Each Ni^{II} ion is in a distorted octahedral environment defined by four N atoms of two chelating phen ligands and two O atoms, one of which comes from a Htfbdc⁻ anion, the other from the μ -tfbdc²⁻ anion. The mean Ni-O bond distance is 0.205 6 nm and the Ni-N bond lengths are averaged to 0.210 0 nm (Table 2).



30% probability ellipsoids; Only the disordered O(3) atom with a site occupancy factor of 0.66 is shown; Symmetry code: A: $-x, 1-y, 1-z$

Fig.1 Molecular structure of **1**

Analysis of the crystal packing of **1**·3H₂O shows that every {[Ni(phen)₂(Htfbdc)]₂(μ -tfbdc)} component is connected to the lattice water molecules through the O-H...O strong hydrogen bonds (Table 3). The adjacent dimeric {[Ni(phen)₂(Htfbdc)]₂(μ -tfbdc)} molecules are linked to form a linear tape along the *a*-axis via a C(18)-H(18A)...O(6G) weak hydrogen bonding interactions and two intermolecular C-F... π interactions employing the fluorine atoms of the Htfbdc⁻ ligands (Fig.2). The C-F... π interactions are described as C-F...Cg (Cg refers to the ring centroid). They can be classified in two groups based on the π -ring system type: Cg1 and Cg3 (pyridyl of the phen ligand) and Cg2 (arene ring of the phen ligand) (Table 4). The distances from the F atoms to the centres of the six-

Table 2 Selected bond lengths (nm) and angles (°) for **1**·3H₂O

Ni(1)-O(1)	0.206 5(6)	Ni(1)-O(5)	0.203 6(6)	Ni(1)-N(1)	0.211 1(6)
Ni(1)-N(2)	0.209 2(6)	Ni(1)-N(3)	0.208 0(6)	Ni(1)-N(4)	0.211 6(6)
O(5)-Ni(1)-O(1)	88.5(3)	O(5)-Ni(1)-N(3)	98.0(2)	O(1)-Ni(1)-N(3)	86.6(2)
O(5)-Ni(1)-N(2)	87.0(2)	O(1)-Ni(1)-N(2)	99.1(2)	O(5)-Ni(1)-N(4)	92.8(2)
N(3)-Ni(1)-N(2)	172.6(2)	O(1)-Ni(1)-N(4)	165.7(2)	N(3)-Ni(1)-N(4)	79.1(2)
N(2)-Ni(1)-N(4)	95.2(2)	O(5)-Ni(1)-N(1)	165.7(2)	O(1)-Ni(1)-N(1)	92.4(3)
N(3)-Ni(1)-N(1)	96.3(2)	N(2)-Ni(1)-N(1)	78.9(2)	N(4)-Ni(1)-N(1)	89.9(2)

Table 3 Hydrogen bond distances and angles for the complexes **1**·3H₂O and **2**·13H₂O

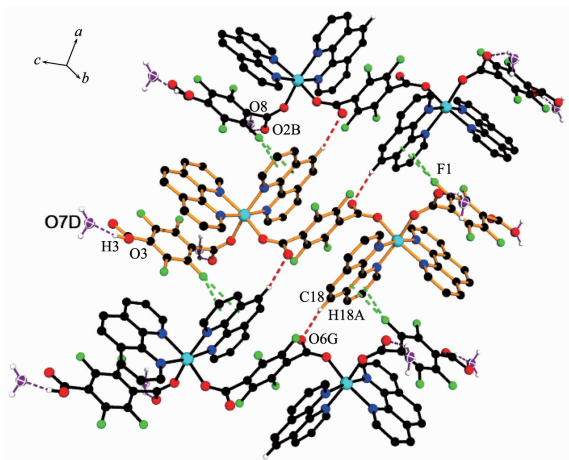
D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	∠ DHA / (°)
1 ·3H ₂ O				
O(8)-H(8Y)···O(2B)	0.082	0.214	0.289 0(17)	146
O(3)-H(3)···O(7D)	0.082	0.177	0.259 3(15)	164
C(9)-H(9A)···O(6F)	0.093	0.252	0.344 2(10)	171
C(18)-H(18A)···O(6G)	0.093	0.255	0.343 6(9)	158
C(21)-H(21A)···O(6H)	0.093	0.234	0.323 3(9)	162
C(3)-H(3B)···F(3I)	0.093	0.245	0.311 6(10)	130
2 ·13H ₂ O				
O(1W)-H(1X)···O(2)	0.085	0.199	0.270 7(5)	141
O(1W)-H(1Y)···O(5A)	0.085	0.200	0.284 0(5)	168
O(3W)-H(3Y)···F(7)	0.085	0.242	0.314 9(5)	144
O(4W)-H(4X)···O(3C)	0.085	0.219	0.286 1(5)	136
O(4W)-H(4Y)···O(8A)	0.085	0.228	0.308 7(6)	159
O(5W)-H(5X)···O(7A)	0.085	0.219	0.278 2(5)	126
O(5W)-H(5Y)···O(6W)	0.085	0.193	0.266 7(5)	145
O(6W)-H(6X)···O(6)	0.085	0.192	0.276 9(5)	172
O(7W)-H(7X)···O(6)	0.085	0.214	0.280 1(5)	134
O(8W)-H(8X)···O(5B)	0.085	0.247	0.299 0(6)	120

Symmetry code for **1**·3H₂O: B: *x*, *y*, *z*-1; D: *x*, *y*+1, *z*; F: -*x*+1, -*y*+2, -*z*+1; G: *x*-1, *y*, *z*; H: -*x*, -*y*+2, -*z*+1; I: -*x*, -*y*+2, -*z*.
 Symmetry code for **2**·13H₂O: A: -1/2+*x*, -1/2+*y*, *z*; B: *x*, 1-*y*, -1/2+*z*; C: *x*, *y*, -1+*z*.

Table 4 C-H... π and C-F... π interactions for the complexes **1**·3H₂O and **2**·13H₂O

C-H/F...Cg	<i>d</i> (C-H/F) / nm	<i>d</i> (H/F...Cg) / nm	<i>d</i> (C...Cg) / nm	∠ C-H/F...Cg / (°)
1 ·3H ₂ O				
C(27)-F(1)···Cg(1C)	0.133	0.307	0.428 1(8)	151
C(27)-F(1)···Cg(2C)	0.133	0.325	0.453 9(8)	163
C(31)-F(4)···Cg(3)	0.136	0.312	0.363 4(8)	101
2 ·13H ₂ O				
C(13)-H(13)···Cg(1)	0.093	0.283	0.362 5(7)	145
C(59)-H(59)···Cg(2)	0.093	0.262	0.355 3(7)	179
C(63)-H(63)···Cg(3E)	0.093	0.262	0.353 8(5)	170
C(49)-H(49)···Cg(5)	0.093	0.288	0.366 1(7)	142
C(23)-H(23)···Cg(6)	0.093	0.259	0.351 9(5)	176
C(27)-H(27)···Cg(7D)	0.093	0.259	0.350 2(6)	168
C(58)-H(58)···Cg(8)	0.093	0.300	0.377 6(6)	142
C(83)-F(6)···Cg(4F)	0.136	0.325	0.379 5(6)	103

Symmetry code for **1**·3H₂O: C: 1+*x*, *y*, *z*. Symmetry code for **2**·13H₂O: D: -1/2+*x*, 1/2+*y*, *z*; E: 1/2+*x*, -1/2+*y*, *z*; F: 1+*x*, *y*, *z*. Cg refers to the ring centre-of-gravity.



Only hydrogen atoms involved in the hydrogen bonds are shown, hydrogen-bond interactions and C-F... π interactions are indicated by dashed lines; O atoms of solvent water molecules are shown in front ellipse pattern; Symmetry code: B: $x, y, z-1$; D: $x, y+1, z$; G: $x-1, y, z$

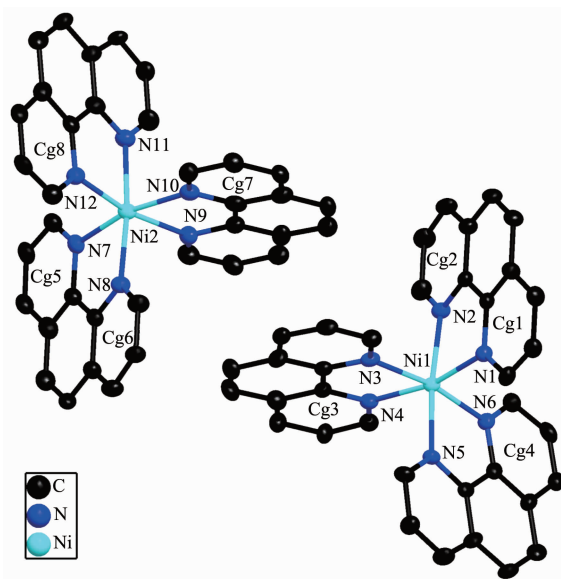
Fig.2 A partial view of the linear tape of the compound $1 \cdot 3\text{H}_2\text{O}$

membered rings (0.307 0(6)~0.325 4(6) nm) agree with the previously reported interval in the copper(II)hexafluoroacetylacetonate (hfacac) complex $[\text{Cu}_3(\text{hfacac})_4(\mu\text{-pyterpy})_2][\text{Cu}(\text{hfacac})_3]_2$ (pyterpy=4'-(3-pyridyl)-2,2':6', 2''-terpyridine) (0.313 5(5)~0.351 9(5) nm)^[18]. In addition, the neighbouring 1D taps are connected by C-H...O weak hydrogen bonds to form a 2D layer. Finally, in the function of the C-H...F weak hydrogen bonds (C(3)...F(3I)=0.311 6(10) nm), a 3D network was formed. The interplanar distances between the arene rings of the $\text{tfbdc}^{2-}/\text{Htfbdc}^-$ anions and the chelating phen planes fall within the range 0.35~0.37 nm, indicating the existence of the significant π - π interactions.

2.4 Structure description for $[\text{Ni}(\text{phen})_3]_2(\text{tfbdc})_2 \cdot 13\text{H}_2\text{O}$ ($2 \cdot 13\text{H}_2\text{O}$)

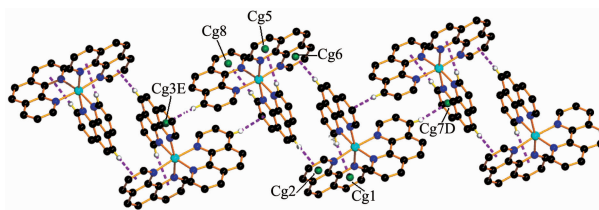
$2 \cdot 13\text{H}_2\text{O}$ crystallizes in the monoclinic space group Cc and the asymmetric unit contains two independent $[\text{Ni}(\text{phen})_3]^{2+}$ cations, two tfbdc^{2-} anions, eight and ten halves of solvent water molecules. As shown in Fig.3, the Ni^{II} ion is coordinated by three phen organic ligands via a typical N, N' -chelating coordination fashion, leading to a distorted $\{\text{NiN}_6\}$ octahedral coordination geometry. These $[\text{Ni}(\text{phen})_3]^{2+}$ cations are connected through seven C-H... π

interactions employing the hydrogen atoms of the phen ligands. The C-H... π interactions are described as C-H...Cg (Cg refers to the ring centroid of the pyridyl of the phen ligand). The distances from the H atoms to the centres of the six-membered rings fall within the range 0.259~0.300 nm (Table 4). Each cation interacts with its upward/downward neighbors to form an infinite 1D $[\text{Ni}(\text{phen})_3]^{2+}$ cationic chain (Fig.4).



30% probability ellipsoids; All hydrogen atoms are omitted for clarity

Fig.3 Perspective view of the cations of **2**

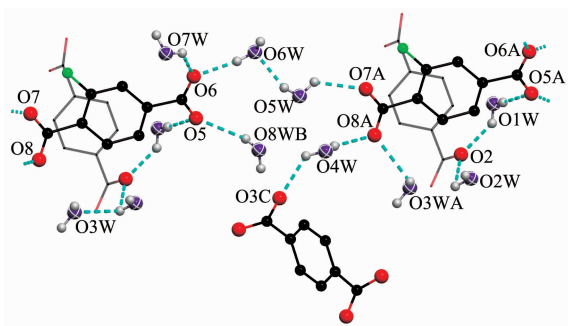


Ring centroids of the arene ring and the pyridyl of the phen ligands are shown in green ball; Only the hydrogen atoms involved in the C-H... π interactions are shown; Symmetry code: D: $-1/2+x, 1/2+y, z$; E: $1/2+x, -1/2+y, z$

Fig.4 Close packing of cationic $[\text{Ni}(\text{phen})_3]^{2+}$ fragments in **2**, emphasizing the C-H... π interactions

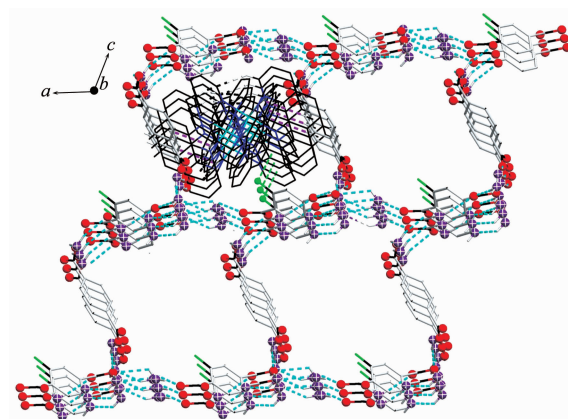
Both tfbdc^{2-} anions act as counter anions and do not participate in coordination. And the carboxylate oxygen atoms (O(2), O(3), O(5), O(6), O(7) and O(8)) of tfbdc^{2-} ligands are all hydrogen bonded to the solvent water molecules (Fig.5). (Ten halves of solvent water molecules are not discussed about the hydrogen bond interactions.) The O...O distances are in the

range of 0.266 7 (5)~0.308 7 (6) nm (Table 3), and most of them are less than the sum of their van der Waals radii (0.304 nm). In addition, this structure contains a hydrogen bonding between the water molecules ($O(5W) \cdots O(6WA)$ 0.266 7(5) nm). In the function of all these hydrogen bond interactions, eight solvent water molecules and both free $tfbdc^{2-}$ anions form an infinite 3D hydrogen-bonded water-carboxylate anions framework (Fig.6). Unlike the 1D tapes formed via $C-F \cdots \pi$ interactions in $1 \cdot 3H_2O$, the similar 1D cationic chains obtained through $C-H \cdots \pi$ interactions were encapsulated in the channels of the above 3D framework through a single $C-F \cdots \pi$ interaction, $C(83)-F(6) \cdots Cg(4)$ ($1+x, y, z$), leading to the final 3D structure. Normally, water clusters locate in organic molecular hosts or inorganic-organic hybrid frameworks. In this case, these water molecules play a



For clarity, only the hydrogen atoms and fluorine atoms involved in the represented interactions are shown; $O-H \cdots O$ hydrogen bond interactions are indicated by dashed lines; Symmetry code: A: $-1/2+x, -1/2+y, z$; B: $x, -y, 1/2+z$; C: $x, 1-y, -1/2+z$

Fig.5 Perspective view of the hydrogen-bond interactions between the solvent water molecules (in front ellipse pattern) and carboxylate anions in $2 \cdot 13H_2O$



For clarity, only the hydrogen atoms and fluorine atoms involved in the represented interactions are shown. $C-H \cdots \pi$, $C-F \cdots \pi$ and $O-H \cdots O$ hydrogen bonds interactions are indicated by dashed lines

Fig.6 A perspective view showing the 3D hydrogen-bonded water-carboxylate anions host framework encapsulating cationic "guest" (only one shown) in the channels in $2 \cdot 13H_2O$

crucial role for forming and stabilizing the 3D hydrogen-bonded water-carboxylate anions host framework. A large number of water structures from 0D water cluster to 3D water structure are summarized and discussed by several reviews^[19-22], however, much less is known about a 3D hydrogen-bonded water-carboxylate anions framework formed via water clusters and anions as a "host" to encapsulate 1D metal-organic cationic chains in the crystalline state.

Compound $2 \cdot 13H_2O$ crystallizes in the non-centrosymmetric polar space group Cc . Accordingly, the molecules must show a polar packing by having the same orientation along the polar c axis: the $tfbdc^{2-}$ anions involved in the $C-F \cdots \pi$ interactions are all point in the same direction (along the polar c axis),

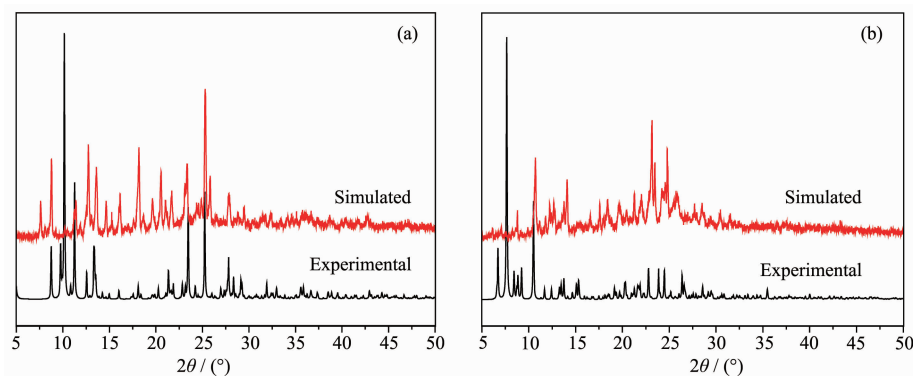


Fig.7 PXRD spectra of (a) $1 \cdot 3H_2O$ and (b) $2 \cdot 13H_2O$

and the other tfbdc^{2-} anions are all point along the polar c axis in Fig.6.

2.5 Powder X-ray diffraction

In order to check the phase purity of $\mathbf{1} \cdot 3\text{H}_2\text{O}$ and $\mathbf{2} \cdot 13\text{H}_2\text{O}$, the powder X-ray diffraction (PXRD) pattern was recorded at room temperature. As shown in Fig.7, the experimental PXRD pattern for each complex correlates well with its simulated one generated from single-crystal X-ray diffraction data, confirming the phase purity of the bulk materials

3 Conclusion

In summary, the complexes $\mathbf{1} \cdot 3\text{H}_2\text{O}$ and $\mathbf{2} \cdot 13\text{H}_2\text{O}$ both contain a combination of $\text{tfbdc}^{2-}/\text{Htfbdc}^-$ and phen ligands but have a remarkable structural and compositional diversity that is achieved in part by the different functions of the anions of H_2tfbdc ligands, coordinated with the Ni^{II} ions in $\mathbf{1}$ while acted as counter anions in $\mathbf{2}$. In $\mathbf{1} \cdot 3\text{H}_2\text{O}$, the 3D network is formed via $\text{C}-\text{H} \cdots \text{O}/\text{F}$, $\text{C}-\text{F} \cdots \pi$ and $\pi \cdots \pi$ interactions. While in $\mathbf{2} \cdot 13\text{H}_2\text{O}$, an unusual 3D hydrogen-bonded water-carboxylate anions framework acting as “host” to encapsulate the 1D metal-organic cationic “guest” is obtained by the $\text{O}-\text{H} \cdots \text{O}$, $\text{C}-\text{H}/\text{F} \cdots \pi$ and $\pi \cdots \pi$ interactions.

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