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Syntheses and structures of three chiral complexes derived from nucleophilic addition of L-proline to di-2-pyridyl ketone

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In the presence of nickel acetate, a chiral ligand, (S)-Hdphp ((S)-N-[di(2-pyridyl)-hydroxy-methyl]-proline), was synthesized *in situ* by nucleophilic addition of L-proline to di-2-pyridyl ketone. Based on this ligand, three chiral mononuclear complexes, {Ni[(S)-dphp](DMF)(H_2O)}(ClO_4) (**1**), {Ni[(S)-dphp](H_2O)_2}(ClO_4)(H_2O)_{1.5} (**2**), and {Ni[(S)-dphp](SCN)(H_2O)} (**3**), have been obtained and characterized by single-crystal X-ray diffraction, elemental analyses, and infrared spectra. By virtue of charge-assisted O–H···O hydrogen-bonding interactions, all the complexes possess double chain structures. The double chains were connected into 2-D networks *via* $\pi \cdots \pi$ stacking and CH···π interactions in **1**. For **2**, O–H···O hydrogen-bonding interactions between free water molecules and other oxygens as well as $\pi \cdots \pi$ stacking and CH···π interactions extend the chains into a 3-D network. Complex **3** exhibits 3-D structure *via* O–H···S interactions.

Keywords: Nucleophilic additions; Chiral; Hydrogen-bonding interactions

1. Introduction

Metal salts play an important role in organic reactions, providing efficient synthetic pathways for synthesis making difficult reactions occur. Metal salts also have a role in synthesizing coordination polymers, and some novel structures have been synthesized through simple one-pot reactions which involve metal-assisted *in situ* ligand syntheses [1, 2].

Reaction involving a nucleophilic addition of secondary-amine to ketone is usually the first step of successive reactions in organic synthetic chemistry. Intermediates are commonly unstable and then dehydrate to obtain imines (Schiff base) or enamines. The reaction has been observed in many cyclization reactions [3–7] but is very rare in acylization [8–10]. In our work, in the presence of nickel acetate, we use L-proline as

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(*S*)-Hdphp
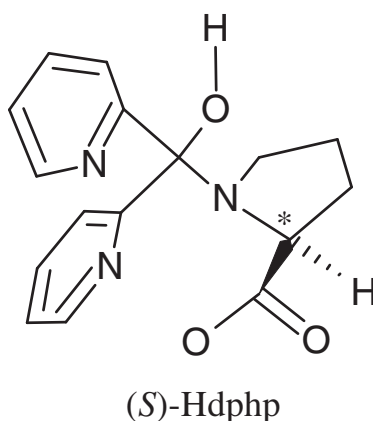
Scheme 1. The ligand diagram.

a nucleophilic agent to react with di-2-pyridine ketone to obtain ligand *in situ*. By this means, we have prepared and characterized two chiral tetranuclear isomorphous complexes, $\{Na[M_4L_3(OAc)_3](ClO_4)_{1.5}(H_2O)_{1.5}\}(ClO_4)(OH)_{0.5} \cdot 3H_2O$ (M = Co, Ni, HL = $(C_5NH_4)_2C(OH)(C_4NH_7CO_2H)$) [11]. Here based on the same ligand (*S*)-Hdphp ((*S*)-Hdphp = (*S*)-N-[di(2-pyridyl)-hydroxy-methyl]-proline, scheme 1), we report three mononuclear complexes, $\{Ni[(S)\text{-dphp}](DMF)(H_2O)\}(ClO_4)$ (**1**), $\{Ni[(S)\text{-dphp}](H_2O)_2\}(ClO_4)(H_2O)_{1.5}$ (**2**), and $\{Ni[(S)\text{-dphp}](SCN)(H_2O)\}$ (**3**). Complexes **1**, **2**, and **3** all exhibit double chain structures through hydrogen-bonding interactions, and are further connected into 2-D or 3-D network *via* $\pi \cdots \pi$ stacking (CH $\cdots \pi$) or hydrogen-bonding interactions.

2. Experimental

Caution: Perchlorate complexes of metal ions are potentially explosive. Only a small amount of material should be prepared and it should be handled with caution.

2.1. *Materials and methods*

$La(ClO_4)_3 \cdot 6H_2O$ (0.5 mol L^{-1}) was synthesized by dissolving lanthanide oxide in an excess of perchloric acid. Di-2-pyridyl ketone (dpk) (98%) and L-proline (99+%) were purchased from ACROS. Other chemicals were used as purchased with A.R. grade. Infrared (IR) spectra were recorded on a Nicolet Magna 750 FT-IR spectrophotometer using KBr pellets from 400 to 4000 cm^{-1}. Elemental analyses (C, H, and N) were performed *via* Vario EL III Etro Elemental Analyzer.

2.2. *Syntheses of the complexes*

2.2.1. {**Ni[(S)-dphp](DMF)(H$_2$O)**}(**ClO$_4$**) (**1**). A 10 mL DMF solution of Ni(OAc)$_2$·4H$_2$O (0.3214 g, 1.3 mmol), di-2-pyridylketone (0.1842 g, 1 mmol), and L-proline (0.1152 g, 1 mmol) was refluxed for 1 h with stirring. After cooling, the mixture was added to NaClO$_4$·H$_2$O (0.2100 g, 1.5 mmol). The blue solution was left at ambient temperature for 2 weeks to obtain 0.22 g blue prism crystals (40.2%, based on di-2-pyridylketone). (Found (%)): C, 41.38; H, 4.49; N, 10.01. Calcd for C$_{19}$H$_{25}$ClN$_4$NiO$_9$ (%): C, 41.68; H, 4.60; N, 10.23). IR (KBr pellet, cm^{-1}): v(NH) 3441, v(OH) 3112, v(CH) 2960, 2891, v(C=O) 1655, v(C–O) 1601, 1417, v(py) 1443, 1387, 1030, 794, 768, 686, 666, v(ClO$_4^-$) 1089, 623.

2.2.2. {**Ni[(S)-dphp](H$_2$O)$_2$**}(**ClO$_4$**)(**H$_2$O**)$_{1.5}$ (**2**). A 20 mL CH$_3$CH$_2$OH/H$_2$O (1:1, v/v) solution of Ni(OAc)$_2$·4H$_2$O (0.3214 g, 1.3 mmol), di-2-pyridylketone (0.1842 g, 1 mmol), and L-proline (0.1152 g, 1 mmol) was refluxed at about 100°C for 1 h with stirring. After cooling, the mixture was added to aqueous solution (4 mL) of La(ClO$_4$)$_3$·6H$_2$O (0.5 mol L^{-1}). The blue solution was left at ambient temperature for 2 weeks to obtain 0.13 g blue prism crystals (25.0%, based on di-2-pyridylketone). (Found (%)): C, 36.81; H, 4.48; N, 7.85. Calcd for C$_{16}$H$_{23}$ClN$_3$NiO$_{10.50}$ (%): C, 36.99; H, 4.46; N, 8.09). IR (KBr pellet, cm^{-1}): v(NH) 3496, v(OH) 3216, v(CH) 2982, 2892, v(C–O) 1603, 1415, v(py) 1464, 1447, 1025, 785, 766, 687, 668, v(ClO$_4^-$) 1086, 624.

2.2.3. {**Ni[(S)-dphp](SCN)(H$_2$O)**} (**3**). **2** (0.2570 g, 0.5 mmol) dissolved in 5 mL DMF with stirring about 20 min was added to a 10 mL CH$_3$CN solution of KSCN (0.9718 g, 1 mmol). After stirring for an additional 30 min, the mixture was filtered and 0.12 g blue prism crystals **3** were obtained 2 weeks later (55.4%, based on **2**) (Found (%)): C, 46.81; H, 4.23; N, 12.65. Calcd For C$_{17}$H$_{18}$N$_4$NiO$_4$S (%): C, 47.14; H, 4.19; N, 12.94). IR (KBr pellet, cm^{-1}): v(NH) 3407, v(OH) 3156, v(CH) 2952, 2890, v(C≡N) 2106, v(C–O) 1593, 1404, v(py) 1463, 1450, 1023, 787, 774, 683, 665.

2.3. *X-ray crystallography*

X-ray single crystal data were collected at 293(2) K (for **1** and **2**) on a MERCURY-CCD area-detector diffractometer, and at 293(2) K on a Siemens SMART-CCD area-detector diffractometer (for **3**) with Mo-Kα radiation ($\lambda = 0.71073$ Å). Data reductions and absorption corrections of **1** and **2** were made with Multi-scan type, while those of **3** were performed with SMART and SADABS software. These structures were solved by direct methods using SHELXS-97 [12] and refined by full-matrix least-squares using SHELXL-97 [13]. Anisotropic displacement parameters were refined for all non-hydrogen atoms. Hydrogens binding to C and hydroxyl-O were added in the riding mode and those of some water molecules were located from the difference Fourier maps. In the structure of **2**, the ClO$_4^-$ is disordered, resolved by two disordered groups with occupancy of 0.5 each. The crystal data and refinement details for the three complexes are listed in table 1.

Table 1. Crystal data and refinement details for **1**–**3**.

	1	**2**	**3**
Empirical formula	$C_{19}H_{25}ClN_4NiO_9$	$C_{16}H_{23}ClN_3NiO_{10.50}$	$C_{17}H_{18}N_4NiO_4S$
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$C2$	$C2$	$P2(1)2(1)2(1)$
Unit cell dimensions (Å, °)			
a	21.149(7)	24.185(2)	9.0639(6)
b	9.652(3)	9.1804(7)	12.5843(8)
c	14.231(5)	10.0455(9)	16.2259(10)
β	124.181(3)	107.362(4)	90
Volume (Å^3), Z	2403.2(14), 4	2128.7(3), 4	1850.8(2), 4
Formula weight	547.59	519.53	433.12
Calculated density, ρ (Mg m^{-3})	1.513	1.621	1.554
Absorption coefficient, μ (mm^{-1})	0.974	1.099	1.192
$F(000)$	1136	1076	896
Reflections measured	9248	8242	9415
Independent reflections	4761	4624	3259
R(int)	0.0176	0.0204	0.0586
GOOF	1.025	1.003	1.280
Flack parameter	−0.0014(16)	0.002(9)	0.05(3)
R^a	0.0434	0.0262	0.0586
Rw^b	0.1151	0.0585	0.1107

1, $a = 0.0781$, $b = 0.0000$; **2**, $a = 0.0236$, $b = 0.0000$; **3**, $a = 0.0186$, $b = 3.6271$.
$^aR = \sum(\|F_o| - |F_c\|)/\sum|F_o|$, $^bRw = \{\sum w[(F_o^2 - F_c^2)^2]/\sum w[(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = (F_o^2 + 2F_c^2)/3]$.

3. Results and discussion

3.1. *Synthesis*

In modern organic synthesis, it is important to synthesize optically pure compounds starting from the appropriate chiral source. Herein, in the presence of nickel acetate, we use L-proline as precursor, which upon addition to di-2-pyridyl ketone gives (S)-Hdphp *in situ*, which is reported only once [11]. We have tried our best to obtain the ligand without metal ion, but without success. By replacement of nickel acetate with copper acetate or other acetate, some experiments have been made but not giving similar complexes with chiral (S)-Hdphp as the ligand. Thus, the reaction is metal assisted.

3.2. *The structure of 1 and 2*

The crystal structure of **1** comprises one mononuclear cation Ni[(S)-dphp] $(DMF)(H_2O)^+$ (figure 1) and counteranion ClO_4^-, but **2** is composed of a mononuclear cation Ni[(S)-dphp]$(H_2O)_2^+$ (figure 2), counteranion ClO_4^-, and one and a half free water molecules. Ni(II) exhibits a slightly distorted octahedron and is chelated by three nitrogens and one oxygen from (S)-dphp$^-$; it is also coordinated to two oxygens, one from water and one from DMF in **1**, and two water molecules in **2**. The chiral (S)-dphp$^-$ retains S conformation and here is tetradentate ($\mu_1 : \eta^1 : \eta^1 : \eta^1 : \eta^1$, scheme 2) to coordinate. Two oxygens from carboxyl and hydroxyl do not coordinate. The Ni–N distance is 2.073(3)–2.096(3) Å for **1** and 2.0797(18)–2.0925(19) Å for **2**, while Ni–O length is 2.037(2)–2.062(3) Å for **1** and 2.0240(13)–2.077(2) Å for **2** (table 2).
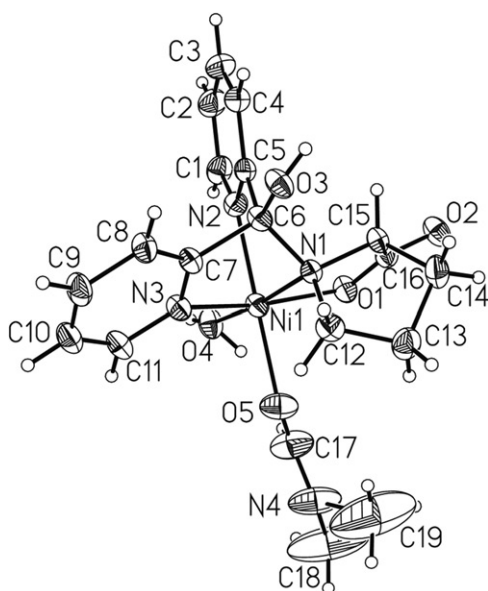
Figure 1. ORTEP plot of the cation in **1** with atom labeling and thermal ellipsoids drawn at 30% probability.
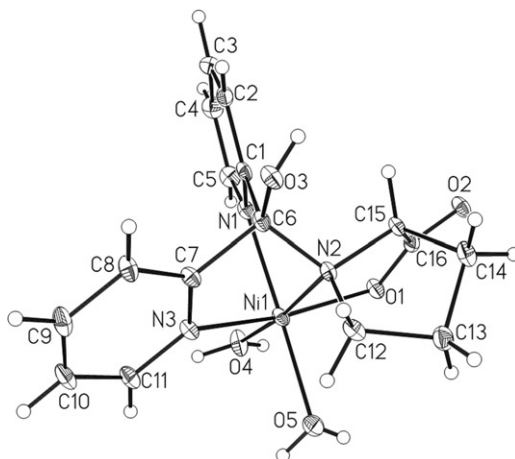
Figure 2. ORTEP plot of the cation in **2** with atom labeling and thermal ellipsoids drawn at 30% probability.

Neighboring mononuclear species are alternately arranged into a double chain by strong hydrogen-bonding interactions along the *b*-axis. Uncoordinated O(2) of COO^- serves as a H-acceptor and interacts with hydroxyl-O(3) (H-donor), which drives the formation of a left-handed (*M*) helical chain (the $O(3) \cdots O(2)$ separations are 2.624(4) Å for **1**, 2.614(2) Å for **2**, table 3, figure 3a). Hydrogen-bonding interaction of O(2) and ligated $H_2O(4)$ forms one right-handed (*P*) helical chain (the $O(4) \cdots O(2)$
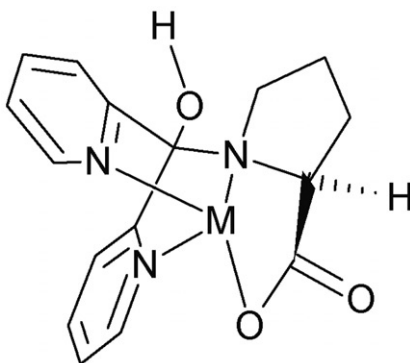
Scheme 2.   Coordination mode of the ligand to metal.

Table 2.   Selected bond lengths (Å) and angles (°) for **1–3**.

1			
Ni(1)–O(1)	2.037(2)	Ni(1)–O(4)	2.061(3)
Ni(1)–O(5)	2.062(3)	Ni(1)–N(2)	2.073(3)
Ni(1)–N(1)	2.082(3)	Ni(1)–N(3)	2.096(3)
O(1)–Ni(1)–O(4)	93.43(11)	O(1)–Ni(1)–O(5)	90.93(13)
O(4)–Ni(1)–O(5)	90.42(14)	O(1)–Ni(1)–N(2)	90.26(11)
O(4)–Ni(1)–N(2)	92.24(13)	O(5)–Ni(1)–N(2)	177.01(13)
O(1)–Ni(1)–N(1)	82.70(10)	O(4)–Ni(1)–N(1)	172.14(12)
O(5)–Ni(1)–N(1)	96.45(13)	N(2)–Ni(1)–N(1)	80.98(12)
O(1)–Ni(1)–N(3)	161.24(11)	O(4)–Ni(1)–N(3)	104.82(13)
O(5)–Ni(1)–N(3)	93.23(14)	N(2)–Ni(1)–N(3)	84.79(12)
N(1)–Ni(1)–N(3)	78.66(12)	–	–
2			
Ni(1)–O(1)	2.0240(13)	Ni(1)–O(4)	2.0419(17)
Ni(1)–O(5)	2.077(2)	Ni(1)–N(3)	2.0797(18)
Ni(1)–N(2)	2.0888(19)	Ni(1)–N(1)	2.0925(19)
O(1)–Ni(1)–O(4)	94.40(7)	O(1)–Ni(1)–O(5)	192.76(8)
O(4)–Ni(1)–O(5)	89.12(8)	O(1)–Ni(1)–N(3)	162.52(6)
O(4)–Ni(1)–N(3)	102.41(7)	O(5)–Ni(1)–N(3)	92.26(8)
O(1)–Ni(1)–N(2)	82.98(6)	O(4)–Ni(1)–N(2)	172.20(7)
O(5)–Ni(1)–N(2)	98.33(8)	N(3)–Ni(1)–N(2)	79.73(7)
O(1)–Ni(1)–N(1)	89.56(6)	O(4)–Ni(1)–N(1)	92.51(7)
O(5)–Ni(1)–N(1)	177.06(8)	N(3)–Ni(1)–N(1)	85.00(7)
N(2)–Ni(1)–N(1)	80.15(7)	–	–
3			
Ni(1)–N(2)	2.016(5)	Ni(1)–O(1)	2.030(4)
Ni(1)–N(3)	2.089(5)	Ni(1)–N(4)	2.107(5)
Ni(1)–N(1)	2.109(4)	Ni(1)–O(4)	2.115(5)
N(2)–Ni(1)–O(1)	99.7(2)	N(2)–Ni(1)–N(3)	98.9(2)
O(1)–Ni(1)–N(3)	161.25(17)	N(2)–Ni(1)–N(4)	92.1(2)
O(1)–Ni(1)–N(4)	90.48(17)	N(3)–Ni(1)–N(4)	86.37(19)
N(2)–Ni(1)–N(1)	170.65(19)	O(1)–Ni(1)–N(1)	82.46(17)
N(3)–Ni(1)–N(1)	78.8(2)	N(4)–Ni(1)–N(1)	78.73(18)
N(2)–Ni(1)–O(4)	92.3(2)	O(1)–Ni(1)–O(4)	89.17(17)
N(3)–Ni(1)–O(4)	92.55(19)	N(4)–Ni(1)–O(4)	175.6(2)
N(1)–Ni(1)–O(4)	96.83(19)	–	–

Table 3.　Important hydrogen-bonding interactions present in **1**–**3**.

D–H$\cdots$A	H$\cdots$A (Å)	D$\cdots$A (Å)	D–H$\cdots$A (°)
1			
O4–H4B$\cdots$O2#1[a]	2.15(6)	2.746(4)	125(6)
O3–H3B$\cdots$O2#2[a]	1.85	2.624(4)	158
2			
O5–H5B$\cdots$O6	1.85(4)	2.734(3)	172(3)
O3–H3B$\cdots$O2#1[a]	1.81	2.614(2)	165
O4–H4C$\cdots$O2#2[a]	1.867(18)	2.687(2)	170(3)
O6–H[b]$\cdots$O3#3		2.902	
O6–H[b]$\cdots$O6#4		2.816	
3			
O3–H3B$\cdots$O2#1[a]	1.96	2.771(6)	172
O4–H4B$\cdots$O2#2[a]	1.93(4)	2.758(6)	160(9)
O4–H4C$\cdots$S1#3	2.49(3)	3.337(5)	168(7)

D = Donor, A = Acceptor.
Symmetry transformations used to generate equivalent atoms: **1**: #1 $-x+3/2, y+1/2, -z+1$; #2 $-x+3/2, y-1/2, -z+1$;
2: #1 $-x+1/2, y+1/2, -z+1$; #2 $-x+1/2, y-1/2, -z+1$; #3 $x, y-1, z$; #4 $1-x, y, 1-z$; **3**: #1 $x-1/2, -y+3/2, -z+1$;
#2 $x+1/2, -y+3/2, -z+1$; #3 $-x+2, y+1/2, -z+3/2$.
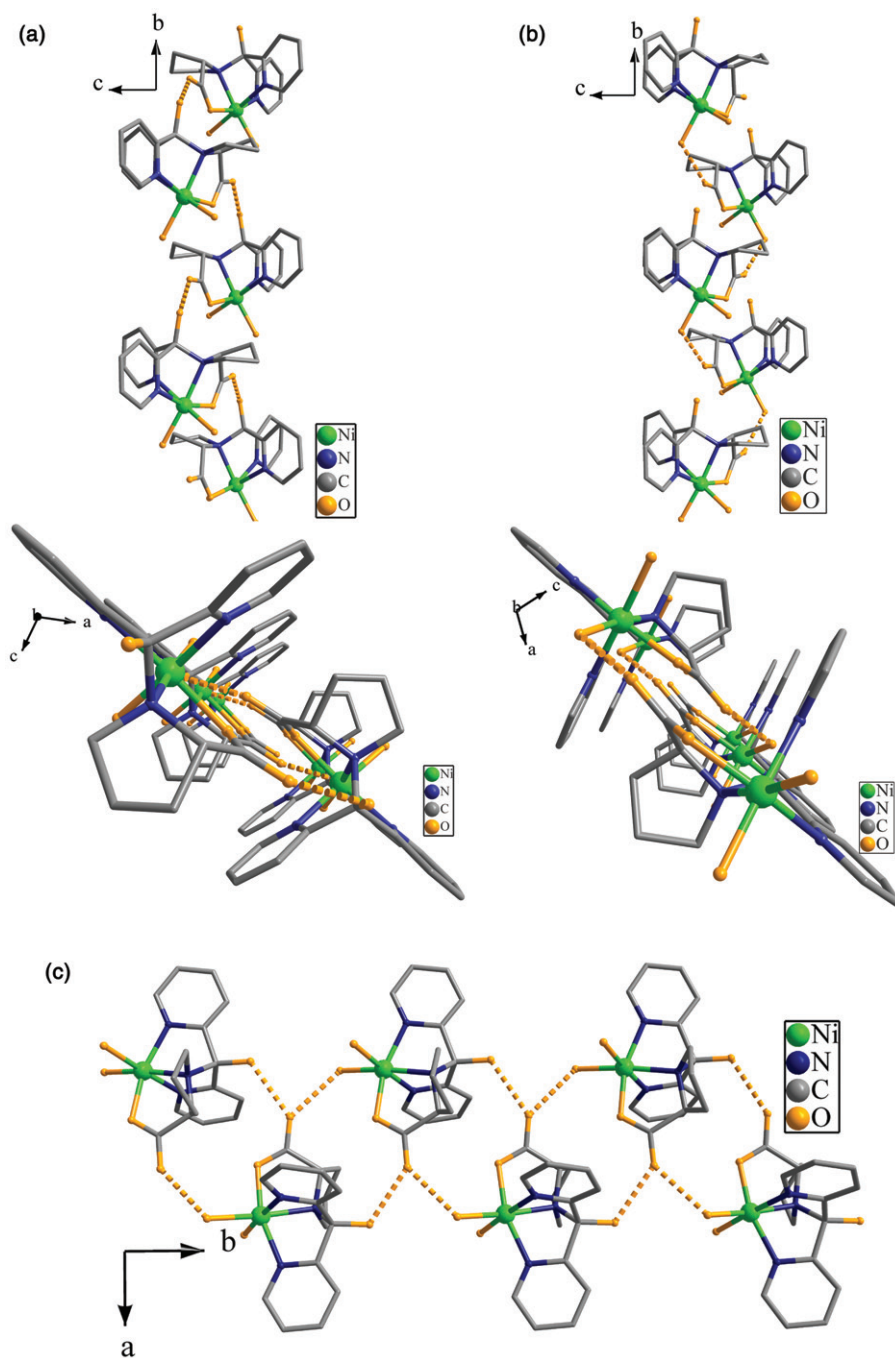[a]Charge-assisted hydrogen-bonds.
[b]Hydrogen atom(s) of water molecules not located.

separations of 2.746(4) Å for **1**, 2.687(2) Å for **2**, table 3, figure 3b). Relative to the helical chains of coordination polymers [14, 15], hydrogen-bonding helical chains are seldom reported [16]. Here, O(2) of COO$^-$ as an acceptor carrying negative charge forms charge-assisted hydrogen bonds with O(3) and O(4), which is usually much stronger than hydrogen bonds between neutral atoms. This is why the two hydrogen-bonding interactions are strong [17–19]. As shown in figure 3(c), the two helical chains are not independent, but interwoven into a double chain by sharing the metal center and (S)-dphp$^-$.

For **1**, between two neighboring double chains, $\pi\cdots\pi$ stacking and CH$\cdots\pi$ interactions construct a 2-D network (figure 4). Two adjacent Ni[(S)-dphp](DMF)(H$_2$O)$^+$ species are stacked through offset pyridine–pyridine $\pi\cdots\pi$ stacking (face–face distance of about 3.58 Å, centroid–centroid distance of about 3.79 Å) and CH$\cdots\pi$ interactions (centroid–centroid 4.92 Å, H$\cdots$centroid 2.85 Å), which can be compared with the literature [20, 21].

Different from **1**, **2** contains free water molecules, which exhibit a further complement of hydrogen bonds to construct a 2-D framework. As shown in figure 5(a), adjacent double chains are connected by free water molecules O(6) and O(6)#4 (#4: $1-x, y, 1-z$) through several hydrogen-bonding interactions (O(5)$\cdots$O(6) 2.734(3) Å, O(6)$\cdots$O(3) 2.902 Å, O(6)$\cdots$O(6) 2.816 Å, table 3). However, isolated ClO$_4^-$ and free H$_2$O(15), due to their disorder, prohibit further discussion about related hydrogen bonds. Between two 2-D layers, two adjacent Ni[(S)-dphp](H$_2$O)$_2^+$ species are stacked through offset pyridine–pyridine $\pi\cdots\pi$ stacking (face–face distance of about 3.58 Å, centroid–centroid distance of about 3.83 Å) and CH$\cdots\pi$ interactions (centroid–centroid 4.89 Å, H$\cdots$centroid 3.13 Å), which can be compared with the literature [22]. Thus, these 2-D layers stack into a 3-D network (figure 5b).

Complexes **1** and **2** belong to the same space group *C*2, possessing similar mononuclear structure, but showing different extended networks. The leading reason
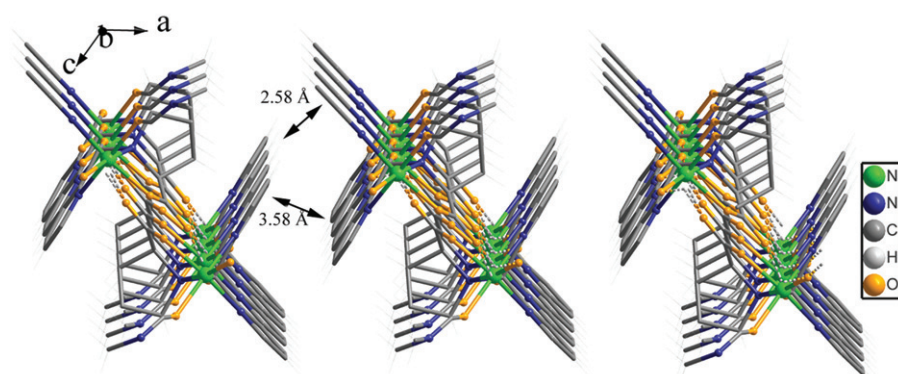
Figure 3. (a) *M*-helical motif in **2**; (b) *P*-helical motif in **2**; (c) double-chain structure in **2**; the charge-assisted hydrogen bonds are indicated as dashed (O(3)···O(2), O(4)···O(2)). Hydrogens are omitted for clarity.

Figure 4.   The packing diagram in **1**; $\pi \cdots \pi$ stacking, and CH$\cdots \pi$ interactions are indicated; intermolecular hydrogen bonds are indicated as dashed (O(3)–H(3B)$\cdots$O(2), O(4)–H(4B)$\cdots$O(2)).

is that **2** has more water molecules (ligated and free) than **1**, increasing hydrogen-bonding interactions, in addition to $\pi \cdots \pi$ stacking, CH$\cdots \pi$ interactions, and other hydrogen-bonding interactions in constructing the 3-D network. For **1**, replacement of one ligated water molecule with one DMF, which does not participate in hydrogen-bonding, only two hydrogen bonds and $\pi \cdots \pi$ stacking, CH$\cdots \pi$ interactions result in a 2-D network.

3.3. *The structure of 3*

Complex **3** is made up of neutral Ni[(S)-dphp](SCN)(H$_2$O) (figure 6). Similar to **1** and **2**, Ni(II) is a distorted octahedral geometry, coordinated to three nitrogens and one oxygen from (S)-dphp$^-$. Additional coordination is from μ_t-SCN$^-$ and H$_2$O. The chiral (S)-dphp$^-$ adopts the same coordination mode as **1**. Bond distances of Ni–N and Ni–O are 2.016(5)–2.109(4) Å and 2.030(4)–2.115(5) Å, respectively (table 2).

Similar to **1** and **2**, double chain structure is formed by neighboring Ni[(S)-dphp](SCN)(H$_2$O) units in inverse fashion *via* hydrogen-bonding interactions (O(3)$\cdots$O(2) 2.771(6) Å, O(4)$\cdots$O(2) 2.758(6) Å, table 3) along the *a*-axis. SCN$^-$ also participates in intermolecular hydrogen-bonding interaction with O(4) (O(4)$\cdots$S(1) 3.337(5) Å, table 3) [23], as shown in figure 7, which serves to link adjacent double chains, resulting in a 3-D network.

Compound **3** belongs to $P2(1)2(1)2(1)$ space group, different from that of **1** and **2**, leading to different packing along axial directions. No $\pi \cdots \pi$ stacking or CH$\cdots \pi$ interactions are found, but SCN$^-$ plays a leading role to construct the 3-D network by intermolecular hydrogen-bonding interaction.

3.4. *IR spectra*

IR spectra are similar for **1–3**. The stretching vibrations of N–H, O–H, and C–H were found from 3500 to 2800 cm^{-1}. Because two CO bonds of –COO$^-$ (dphp$^-$) bring resonance, typical C=O stretching vibrations disappear. For example, in **1** spectral
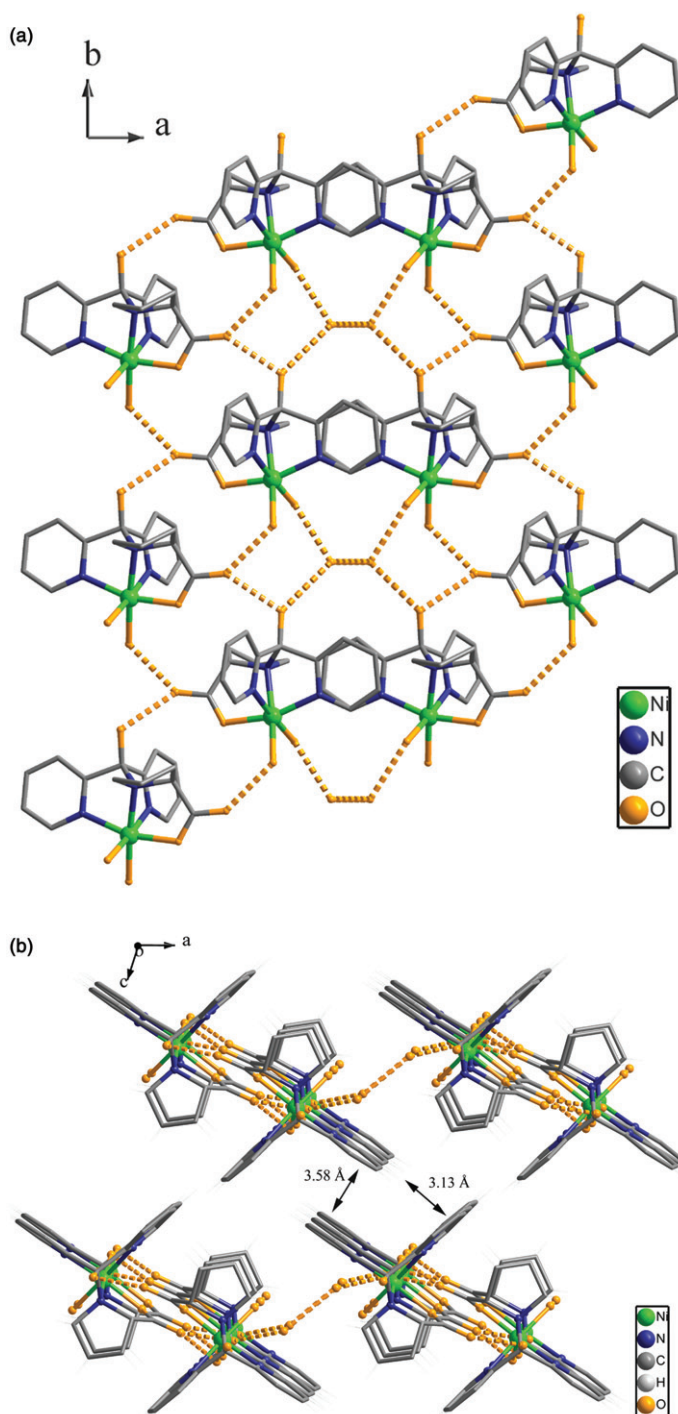
Figure 5. (a) The hydrogen bond motif in **2**; (b) the packing diagram of **2**, $\pi \cdots \pi$ stacking, and $CH \cdots \pi$ interactions are indicated; intermolecular hydrogen bonds are indicated as dashed ($O(3) \cdots O(2)$, $O(4) \cdots O(2)$, $O(5) \cdots O(6)$, $O(6) \cdots O(3)$, $O(6) \cdots O(6A)$). Some hydrogens are omitted for clarity.
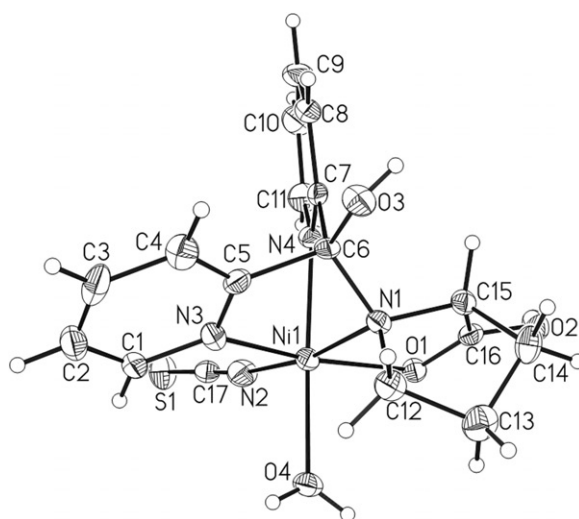
Figure 6.   ORTEP plot of **3** with atom labeling and thermal ellipsoids drawn at 30% probability.

bands at 1601 and 1417 cm^{-1} are, respectively, from asymmetrical and symmetrical vibrations of COO^{-}. Peaks at 1510–1000 cm^{-1} are attributed to pyridyl ring stretching, 660–800 cm^{-1} for the pyridyl ring C–H in-plane vibration and out-of-plane vibrations. For **3**, due to the existence of SCN^{-}, the sharp absorbance at 2106 cm^{-1} should be ascribed to C≡N. The C=O (DMF) strong peak is at 1655 cm^{-1} in **1**. The symmetric and asymmetric vibrations of ClO$_4^-$ are at 1089 and 623 cm^{-1} for **1**, 1086 and 624 cm^{-1} for **2**.

4. Conclusion

In the presence of nickel acetate, a chiral ligand (*S*)-dphp derived from nucleophilic addition of L-proline as a secondary amine to ketone (di-2-pyridylketone) has been synthesized *in situ*, and three chiral mononuclear complexes containing the ligand have been obtained. With O–H$\cdots$O hydrogen-bonding interactions, three complexes exhibit double-chain structures. Compounds **1** and **2** crystallize in the same space group, but small differences in mononuclear structures result in different 3-D or 2-D networks constructed by $\pi\cdots\pi$ stacking (CH$\cdots\pi$) or hydrogen-bonding interactions. Compound **3** belongs to a different space group from **1** and **2**, leading to different 3-D packing through hydrogen-bonding interactions.

Supplementary material

Crystallographic data for the structural analyses reported in this article with CCDC numbers 802015, 802016, and 802017 for **1–3**, respectively, can be obtained free of
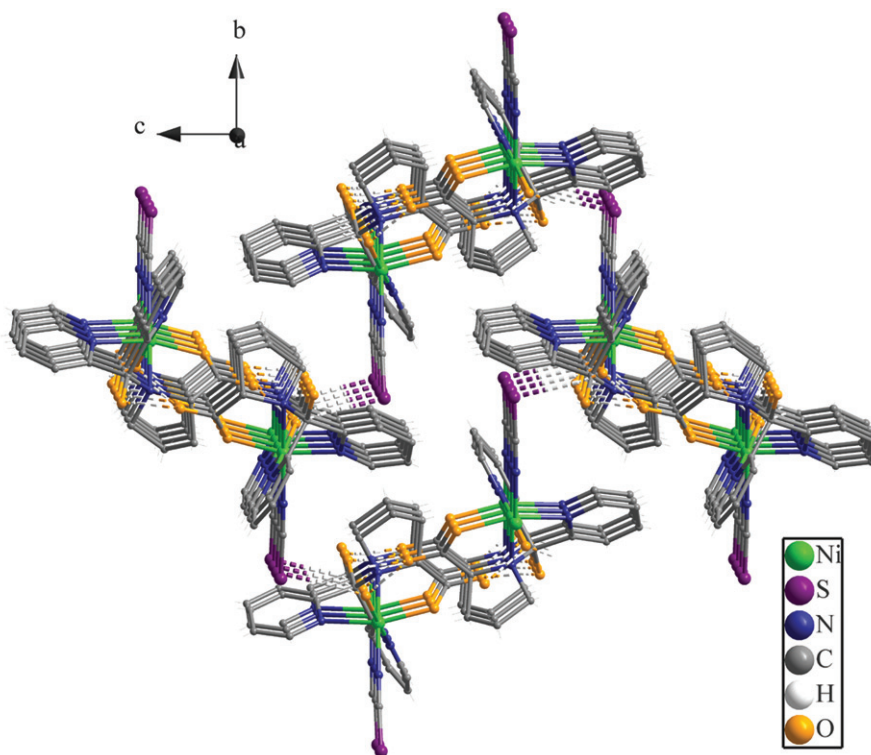
Figure 7.   The 3-D network assembled through hydrogen bonds in **3**; intermolecular hydrogen bonds are indicated as dashed (O(3)–H(3B)···O(2), O(4)–H(4C)···O(2), O(4)–H(4B)···S(1)). Some hydrogens are omitted for clarity.

charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk).

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