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Nickel(II) Coordination Polymers [ndash] 4,4′-Bipyridine-Connected Six- and Four-Fold Metal[ndash]Succinate Helices and Their Corresponding Chiral and Achiral Networks

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The reaction of equimolar amounts of $Ni(NO_3)_2 \cdot 6H_2O$, $Na_2(suc) \cdot 6H_2O$ (suc = succinate) and 4,4′-bipyridine (bipy) under different conditions yield the coordination polymers $[Ni(suc)(bipy)(H_2O)_2]_n \cdot 2nH_2O$ (**1**) and $[Ni(suc)(bipy)(H_2O)_2]_n \cdot nH_2O$ (**2**). The complexes were characterized by elemental analysis, spectroscopic, thermogravimetric, and magnetic susceptibility measurements. Crystal structures reveal that the metal centers in both complexes are in a distorted octahedral N_2O_4 coordination sphere assembled by mutually *trans* pairs of 4,4′-bipyridine, succinate, and water molecules. The helical metal–succinate chains have a right-handed sixfold configuration in **1**, with guest water molecules inside the helix, and both right- and left-handed fourfold configurations in **2**, with guest water molecules outside the helix. The parallel helical substructures are connected by 4,4′-bipyridine and provide 3D chiral $7^5.9$ and achiral $6^5.8$ networks in **1** and **2**, respectively.

Introduction

In the last decade, self-assembled microporous metal–ligand coordination networks have received attention due to their potential application in a vast range of areas such as gas storage, ion exchange, catalysis, separation science, optical and magnetic materials, and sensors.[1–22] In the design of coordination networks, the most popular neutral bridging ligand is the rigid, linear 4,4′-bipyridine molecule (bipy).[20–22] Various dicarboxylates, with or without ancillary ligands, are the most versatile anionic bridging ligand system, which provides diverse types of networks with a variety of metal ions.[18,19,21–27] In these species, the nature of the dicarboxylate ligand plays a crucial role in determining the network topology and the pore size. Among the dicarboxylate ligands, succinate (suc) is particularly attractive as it has three rotamers, namely *eclipsed*, *anti*, and *gauche*, that can generate different networks. In addition, the *gauche* form is chiral and can produce noncentrosymmetric chiral networks. A cobalt(II) coordination polymer, $[Co(suc)(bipy)(H_2O)_2]_n \cdot 2nH_2O$ containing *gauche* suc, synthesized from succinic acid, bipy, and cobalt(II) nitrate under hydrothermal conditions at 160 °C has been reported to form a very interesting chiral network.[25] This complex crystallizes in the space group $P6_522$. Here the left-handed helical Co–suc chains are connected by bipy and a dense chiral twisting $7^5.9$ network is formed. Two structures of the analogous Cu^{II} coordination polymer have been reported in the space groups $P6_1$ and $P6_5$.[23,24] The first complex was synthesized at atmospheric pressure and room temperature in an aqueous medium,[23] whereas the second was prepared under hydrothermal conditions at 150 °C.[24] These two structures are enantiomeric to each other as one contains right-handed and the other left-handed homochiral Cu–suc helices. It has been noted[25] that the space groups of these structures will be $P6_122$ and $P6_522$ and they give the same $7^5.9$ network as observed for the Co^{II} complex. Controlled homochiral synthesis of the Cu^{II} analogue has been demonstrated by varying the pH of the ammonia solution used during its synthesis at atmospheric pressure and room temperature.[26] The shift of the equilibrium for the amine complex formation reaction with the change of pH plays a crucial role in the homochiral isolation of the complex. Similar studies have been undertaken to understand the role of the reaction condition defining variables such as pH, solvent, concentration, temperature, and time in determining the composition and topology of the coordination network generated by a particular combination of reactants.[27] Interestingly, the combination of suc and bipy with Co^{II} and Cu^{II} provides analogous coordination polymers with the same chiral $7^5.9$ network from very different reaction conditions, namely closed hydrothermal conditions at high temperature and open aqueous media at room temperature.[23–26] It appears that this particular polymeric species and the accompanying network are favored by these two bridging ligands irrespective of the reaction conditions and the metal ion. To verify this assumption we have reacted sodium succinate and bipy with Ni^{II} nitrate under various conditions. We have isolated $[Ni(suc)(bipy)(H_2O)_2]_n \cdot 2nH_2O$ (**1**) and the one water molecule deficient repeat unit containing $[Ni(suc)(bipy)(H_2O)_2]_n \cdot nH_2O$ (**2**).

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Herein we describe the synthesis, characterization, physical properties, X-ray structures, and network topologies of **1** and **2**.

Results and Discussion

Reactions of equimolar amounts of $Ni(NO_3)_2 \cdot 6H_2O$, $Na_2(suc) \cdot 6H_2O$, and bipy in both closed and open conditions with variation of the solvent, concentration, time, and temperature have been performed. Crystalline materials suitable for X-ray structure determination have been obtained from two reactions. These are $[Ni(suc)(bipy)(H_2O)_2]_n \cdot 2nH_2O$ (**1**) analogous to the previously reported Co^{II} and Cu^{II} complexes[23–26] and $[Ni(suc)(bipy)(H_2O)_2]_n \cdot nH_2O$ (**2**). Elemental analyses for **1** and **2** are in satisfactory agreement with their proposed formulae. The difference in the concentrations of the reagents needed for the syntheses of **1** and **2** is very small. However, **1** was formed in a closed atmosphere at significantly higher temperature (120 °C) than that (80 °C) needed for the synthesis of **2** in an open atmosphere. The other major difference is in the ratio of dimethylformamide and water used as the solvent mixture for both complexes; the ratio is 1:2 for **1**, and 1:1 for **2**. It is likely that the more aqueous, high temperature, and hence high pressure closed solvothermal synthetic condition assists the repeat unit of **1** to be dihydrated, whereas formation of the monohydrated repeat unit-containing **2** is preferred by the less aqueous reaction mixture at atmospheric pressure and lower temperature.

Thermogravimetric analyses (TGA) of **1** and **2** were performed under flowing nitrogen gas in the temperature range 30–400 °C. The behavior of both complexes is similar. Dehydration starts and ends in the temperature range ca. 70–135 °C. The observed weight losses are 17.8 and 14.3% for **1** and **2**, respectively. These values correspond well with the calculated values of 17.88 and 14.04% for **1** and **2**, respectively. On heating further, decomposition of the dehydrated residue starts at ca. 200 °C and continues beyond 400 °C.

The room temperature (300 K) magnetic moments of the repeat units of **1** and **2** are essentially identical (2.95 and 2.94 μ_B) and indicate the presence of two unpaired electrons per metal center in each case. These values are very close to the spin-only value (2.83 μ_B) expected for octahedral Ni^{II} complexes. We measured the magnetic susceptibility of **1** in the temperature range 25–300 K at a constant magnetic field of 10 kG to explore if there is any spin coupling between the metal centers. The variations of the effective magnetic moment (μ_{eff}) and the inverse molar magnetic susceptibility (χ_M) with temperature (T) are illustrated in Figure 1. The linear χ_M^{-1} vs. T plot indicates that **1** has Curie paramagnetic behavior. The data were fitted using the Curie–Weiss law. The values of C and θ obtained are 1.02 and 2.24, respectively.

The IR spectra of **1** and **2** are essentially identical except for some small shifts. Water appears as a broad strong band centered at ca. 3275 cm^{-1}. The sharp medium intensity band at ca. 1612 cm^{-1} is most likely associated with the bipy ligand. Two strong bands observed at ca. 1538 and ca. 1415 cm^{-1} are attributed to the ν_{asym} and ν_{sym} stretches of the carboxylate groups, respectively.[28]

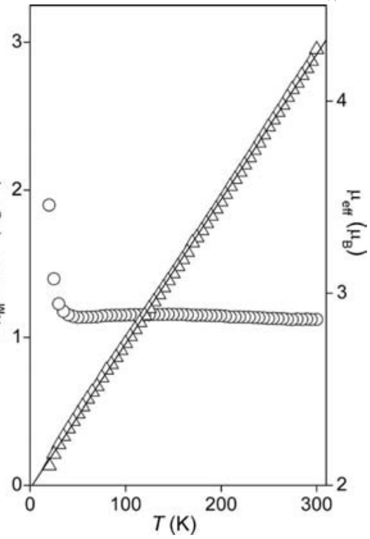


Figure 1. Inverse molar magnetic susceptibility (Δ) and effective magnetic moment (○) of **1** as a function of temperature (T). The solid line represents the linear least-squares fit of the inverse molar magnetic susceptibility vs. T.

The solid state electronic spectra of **1** and **2** are shown in Figure 2. The spectral profiles are very similar and each display four absorption bands. Two weak absorptions are observed in the range 1010–620 nm. Absorptions in this range are commonly observed for octahedral Ni^{II} complexes and are due to d–d transitions.[29,30] The shoulder at 330 nm and the intense band at 270–275 nm are most likely due to charge transfer and ligand centered transitions.

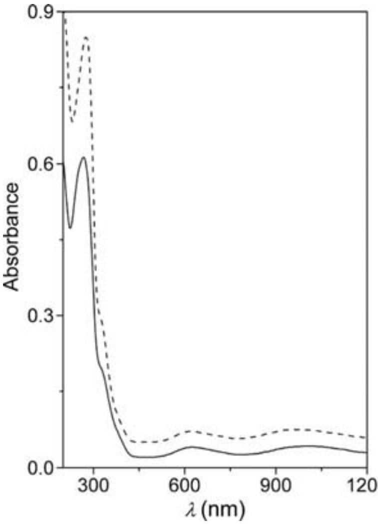


Figure 2. The solid state electronic spectra of **1** (solid line) and **2** (dashed line).

Complex **1** crystallizes in the chiral hexagonal space group $P6_122$, whereas **2** crystallizes in the noncentrosymmetric achiral tetragonal space group $I\bar{4}2d$. The asymmetric unit of **1** contains half each of a Ni atom, suc, and bipy with one coordinated and one uncoordinated water molecule. The asymmetric unit of **2** contains two distinct half occupancy Ni centers, two halves each of suc and bipy, and two coordinated and one uncoordinated water molecule. The bond parameters associated with the metal ions in **1** and **2** are listed in Table 1 and Table 2, respectively. The hydrogen bond parameters involving the water molecules for both complexes are summarized in Table 3. The Flack parameters used to determine the correct absolute configuration/structure[31] of **1** and **2** are given in Table 4. The metal centers are in distorted octahedral all *trans* $(\mathrm{N_{bipy}})_2(\mathrm{O_{suc}})_2(\mathrm{O_{water}})_2$ coordination spheres in both complexes. The bridging bipy and suc ligands form a $\mathrm{N_2O_2}$ square plane and the monodentate water molecules occupy the two axial sites (Figure 3). The *cis* and *trans* bond angles about the metal atoms are in the ranges 87.55(8)–92.48(8)° and 176.25(9)–180°, respectively. The bond lengths associated with the metal atoms in both complexes are within the range reported for Ni^{II} complexes with similar coordinating atoms.[32–39] However, the average Ni–O$_{suc}$ and Ni–N$_{bipy}$ bonds are shorter, and Ni–O$_{water}$ bonds are longer in **1** compared to those in **2** (see Tables 1 and 2). It is possible that these differences in the bond lengths and the variation of the helicity of the Ni–suc chain in the two complexes are due to the high pressure conditions used for the synthesis of **1**.

Table 1. Selected bond lengths [Å] and angles [°] for **1**.[a]

Ni–N(1)	2.072(3)	Ni–N(2)′	2.060(3)
Ni–O(1)	2.049(2)	Ni–O(1)′	2.049(2)
Ni–O(3)	2.136(2)	Ni–O(3)′	2.136(2)
N(1)–Ni–N(2)′	180.0	N(1)–Ni–O(1)	88.27(6)
N(1)–Ni–O(1)′	88.27(6)	N(1)–Ni–O(3)	90.38(7)
N(1)–Ni–O(3)′	90.38(7)	N(2)′–Ni–O(1)	91.73(6)
N(2)′–Ni–O(1)′	91.73(6)	N(2)′–Ni–O(3)	89.62(7)
N(2)′–Ni–O(3)′	89.62(7)	O(1)–Ni–O(1)′	176.54(12)
O(1)–Ni–O(3)	92.48(8)	O(1)–Ni–O(3)′	87.55(8)
O(1)′–Ni–O(3)	87.55(8)	O(1)′–Ni–O(3)′	92.48(8)
O(3)–Ni–O(3)′	179.24(14)		

[a] Symmetry transformations used to generate equivalent atoms: *x* + 1, *y*, *z* for N(2)′ and *x* – *y* + 1, –*y* + 2, –*z* for O(1)′ and O(3)′.

In both **1** and **2**, the water molecules are involved in moderate to strong intra- and intermolecular hydrogen bonds (Table 3). The majority of these hydrogen bonds are of the charge assisted type[40,41,42] as they involve the uncoordinated suc-O atoms as acceptors. In **1**, the uncoordinated suc-O atom (O2) acts as the acceptor in the intra- and intermolecular hydrogen bonds with the metal coordinated (O3) and the uncoordinated lattice (O4) water molecules, respectively. Each of the two uncoordinated water molecules is also involved in a second hydrogen bond as donor with the O atom of the corresponding crystallographically similar water molecule. In **2**, the lattice water molecule (O7) participates in three hydrogen bonds as an acceptor to one of the coordinated water molecules (O6) and as a donor to the crystallographically similar water molecule (O7) and an uncoordinated suc-O atom (O2). The same uncoordinated suc-O atom (O2) also acts as the acceptor in the intramolecular hydrogen bond with the other metal coordinated water molecule (O5). The second uncoordinated suc-O atom (O4) acts as the acceptor in inter- and intramolecular hydrogen bonds with the two coordinated water molecules O5 and O6, respectively (Table 3).

Table 2. Selected bond lengths [Å] and angles [°] for **2**.[a]

Ni(1)–N(1)	2.095(2)	Ni(2)–N(2)	2.101(2)
Ni(1)–N(3)	2.110(2)	Ni(2)–N(4)	2.056(2)
Ni(1)–O(1)	2.0866(15)	Ni(2)–O(3)	2.0763(15)
Ni(1)–O(1)′	2.0866(15)	Ni(2)–O(3)′	2.0763(15)
Ni(1)–O(5)	2.0927(16)	Ni(2)–O(6)	2.0994(16)
Ni(1)–O(5)′	2.0927(16)	Ni(2)–O(6)′	2.0994(16)
N(1)–Ni(1)–N(3)	180.0	N(2)–Ni(2)–N(4)	180.0
N(1)–Ni(1)–O(1)	89.43(4)	N(2)–Ni(2)–O(3)	89.70(4)
N(1)–Ni(1)–O(1)′	89.43(4)	N(2)–Ni(2)–O(3)′	89.70(4)
N(1)–Ni(1)–O(5)	89.21(5)	N(2)–Ni(2)–O(6)	91.87(5)
N(1)–Ni(1)–O(5)′	89.21(5)	N(2)–Ni(2)–O(6)′	91.87(5)
N(3)–Ni(1)–O(1)	90.57(4)	N(4)–Ni(2)–O(3)	90.30(4)
N(3)–Ni(1)–O(1)′	90.57(4)	N(4)–Ni(2)–O(3)′	90.30(4)
N(3)–Ni(1)–O(5)	90.79(5)	N(4)–Ni(2)–O(6)	88.13(5)
N(3)–Ni(1)–O(5)′	90.79(5)	N(4)–Ni(2)–O(6)′	88.13(5)
O(1)–Ni(1)–O(1)′	178.87(8)	O(3)–Ni(2)–O(3)′	179.40(8)
O(1)–Ni(1)–O(5)	90.82(7)	O(3)–Ni(2)–O(6)	92.21(7)
O(1)–Ni(1)–O(5)′	89.17(7)	O(3)–Ni(2)–O(6)′	87.81(7)
O(1)′–Ni(1)–O(5)	89.17(7)	O(3)′–Ni(2)–O(6)	87.81(7)
O(1)′–Ni(1)–O(5)′	90.82(7)	O(3)′–Ni(2)–O(6)′	92.21(7)
O(5)–Ni(1)–O(5)′	178.41(10)	O(6)–Ni(2)–O(6)′	176.25(9)

[a] Symmetry transformation used to generate equivalent atoms O(1)′, O(3)′, O(5)′ and O(6)′: *x*, –*y* + 1/2, –*z* + 1/4.

The bridging suc ligands in **1** are in the chiral right-handed *gauche* conformation. The torsion angle for the skel-

Table 3. Hydrogen bond parameters for **1** and **2**.

Complex	D–H···A [Å]	*d*(D–H) [Å]	*d*(H···A) [Å]	*d*(D···A) [Å]	<(DHA) [°]
1	O(3)–H(3A)···O(2)	0.87(4)	1.80(4)	2.647(3)	166(4)
	O(3)–H(3B)···O(3)[a]	0.69(1)	2.52(1)	3.201(4)	172(4)
	O(4)–H(4A)···O(2)	0.75(7)	2.00(7)	2.751(4)	174(9)
	O(4)–H(4B)···O(4)[b]	0.73(8)	2.29(6)	2.846(14)	134(10)
2	O(5)–H(5A)···O(2)	0.84(3)	1.83(3)	2.662(2)	171(3)
	O(5)–H(5B)···O(4)[c]	0.74(3)	2.01(3)	2.714(2)	158(3)
	O(6)–H(6A)···O(4)	0.86(3)	1.81(3)	2.643(3)	161(3)
	O(6)–H(6B)···O(7)	0.69(3)	2.22(3)	2.906(3)	171(3)
	O(7)–H(7B)···O(2)[c]	0.87(4)	1.85(4)	2.721(3)	176(4)
	O(7)–H(7A)···O(7)[d]	0.76(4)	2.14(4)	2.884(3)	164(4)

[a] Symmetry transformation used to generate equivalent atoms: *x*, *x* – *y* + 2, –*z* + 1/6. [b] –*x* + *y*, *y*, –*z* + 1/2. [c] –*x* + 3/2, *y*, –*z* – 1/4. [d] *y* + 1, –*x* + 1, –*z*.

Table 4. Crystallographic data for **1** and **2**.

Complex	**1**	**2**
Formula	$NiC_{14}H_{20}N_2O_8$	$NiC_{14}H_{18}N_2O_7$
M_w	403.03	385.01
Crystal system	hexagonal	tetragonal
Space group	$P6_122$	$I\bar{4}2d$
a [Å]	11.1996(4)	22.5486(8)
b [Å]	11.1996(4)	22.5486(8)
c [Å]	24.2343(18)	13.2686(9)
α [°]	90	90
β [°]	90	90
γ [°]	120	90
V [Å^3]	2632.5(2)	6746.3(6)
Z	6	16
$\rho_{calcd.}$ [g cm^{-3}]	1.525	1.516
μ [mm^{-1}]	1.149	1.188
Reflections collected	14646	18861
Unique reflections	1731	3337
Reflections observed [$I \geq 2\sigma(I)$]	1566	2995
Parameters	128	240
GOF on F^2	1.056	1.044
$R1$, $wR2$ [$I \geq 2\sigma(I)$]	0.0347, 0.0762	0.0269, 0.0649
$R1$, $wR2$ [all data]	0.0408, 0.0789	0.0318, 0.0671
Flack parameter	–0.02(3)	0.100(11)
max/min $\Delta\rho$ [e Å^{-3}]	0.372/–0.187	0.417/–0.185

eton carbon chain of the suc is 69.7(5)°. This conformation leads to the formation of a right-handed sixfold Ni–suc helix along the crystallographic *c*-axis (Figure 4). In this helical structure, the Ni···Ni distance in the succinato-bridged fragment is 7.20 Å and that of the repeating period of the helix is 21.09 Å. The hydrogen bonded guest water molecules are located on the inner wall of the channel formed by the cylindrical sixfold helix (Figure 4). Each of these homochiral helices is connected to six parallel adjacent helices by the bipy ligands. The interhelical bipy-bridged Ni···Ni distance is 11.20 Å. As a result a hexagonal arrangement of interconnected helices is formed (Figure 5). The perception and description of 3D network topology using nodes and the links between them is a well known and informative methodology.[43,44] In **1**, the tetracoodinated planar Ni nodes formed by the two types of bridging ligand (bipy and suc) and the homochiral 6_1 helical Ni–suc sub-

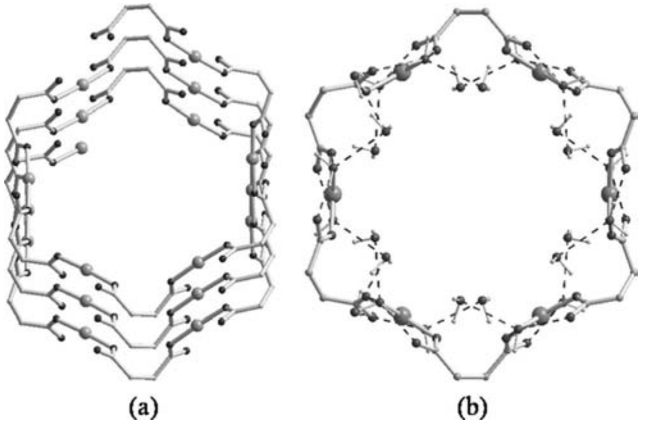


Figure 4. (a) The right-handed sixfold helix formed by the Ni–suc chain and (b) the hydrogen bonded water molecules inside the helix in **1**. Hydrogen atoms of the suc and bipy molecules are omitted for clarity.

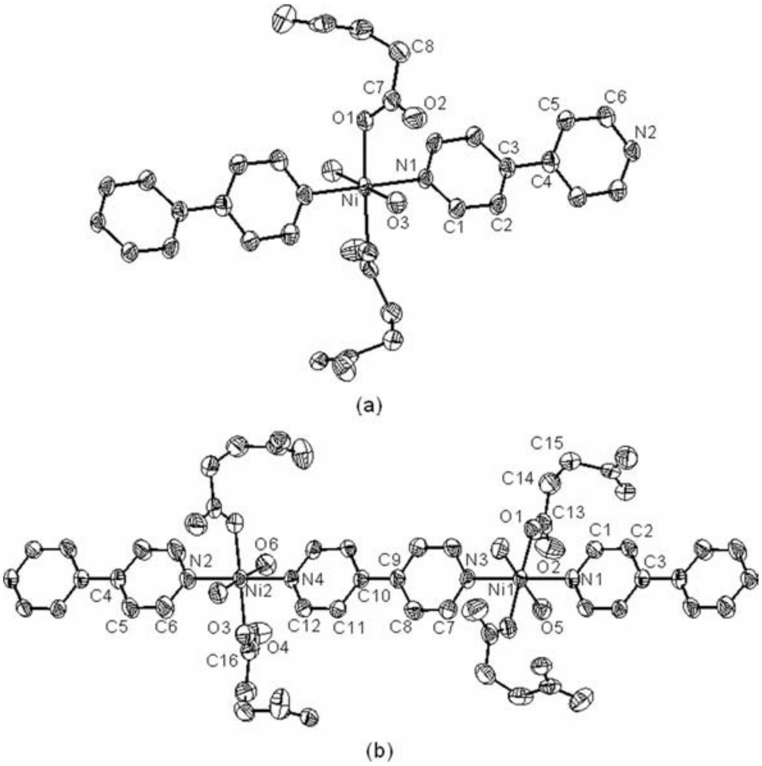
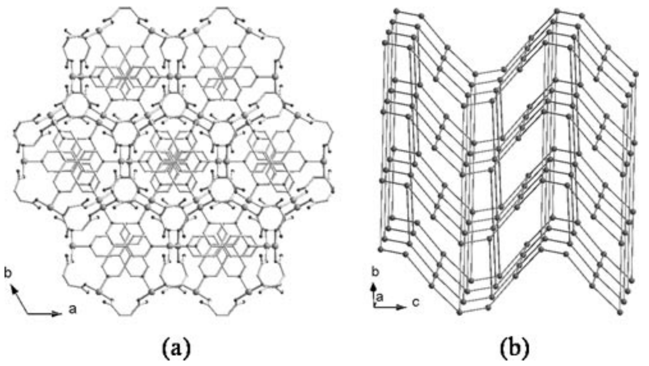


Figure 3. Coordination spheres in (a) **1** and (b) **2** with the atom labeling schemes. For clarity hydrogen atoms and the lattice water molecules are not shown.

structures lead to the dense chiral twisting $7^5.9$ network (Figure 5) identical to that reported for the Co^{II} and Cu^{II} analogues.[25]



(a) (b)

Figure 5. (a) Hexagonal arrangement of bipy-connected homochiral Ni–suc helices (hydrogen atoms and water molecules are omitted for clarity) and (b) the dense twisting $7^5.9$ network formed by **1**.

The structure of **1** shows that there is a spontaneous resolution of one enantiomer in the crystal.[42] To examine whether the bulk material is optically pure or enriched we recorded its circular dichroism (CD) spectrum in KBr. No band was observed in the CD spectrum, indicating that both enantiomers of **1** are present in equal amounts in the bulk material.

The suc ligand in **2** is also in the *gauche* conformation. The torsion angle [69.0(3)°] for the skeleton carbon chain is very similar to that in **1**. However, here the suc ligands exist in both right- and left-handed *gauche* conformations. As a result the Ni–suc chain has both right- and left-handed helical structures. Therefore, **2** is achiral. In **1**, the Ni–suc chains are sixfold helices, and in **2** they exist as fourfold helices (Figure 6). In these fourfold helices, the intrahelical Ni···Ni distance along the succinato bridge is 6.87 Å and that of the repeating period of the helix is 13.27 Å. These values are significantly shorter than those observed in the sixfold Ni–suc helices in **1**. The guest water molecules in **1** are on the inner wall of the cylindrical sixfold helix, whereas in **2** the guest water molecules are on the outer wall of the fourfold helix (Figure 6). In **2**, each helix is connected to four adjacent helices by bipy ligands to form a tetragonal ordering of the parallel helices (Figure 7). The interhelical Ni···Ni distance (11.25 Å) along the bipy bridge is very similar to that of **1**. Although the nodes and the linking ligands are same in **1** and **2**, the network topology of **2** is completely different to that of **1**. In **2**, both right- and left-handed fourfold helical Ni–suc substructures yield an achiral network (Figure 7) very similar to the $6^5.8$ net observed for $CdSO_4$.[45–47] The network in **2** may be described as distorted $6^5.8$ net[47] due to the lack of colinearity in the con-

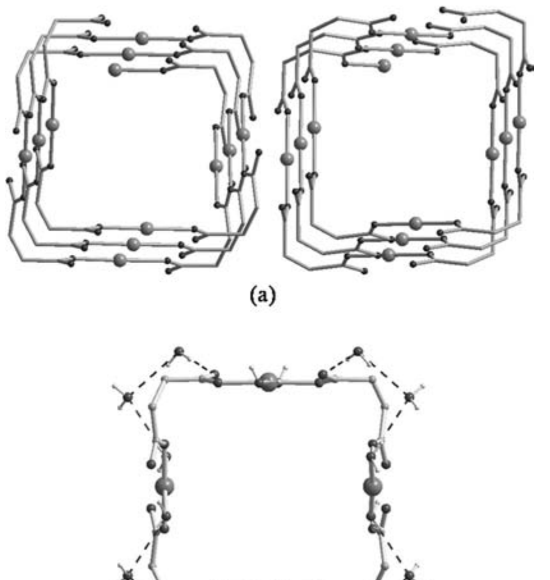
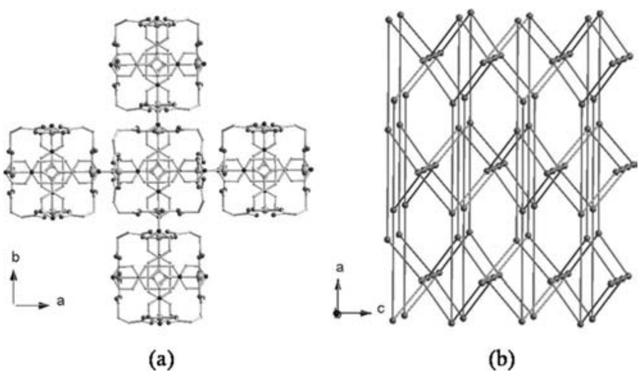

(a)
(b)

Figure 6. (a) The right- and left-handed fourfold adjacent Ni–suc helices and (b) the hydrogen bonded water molecules outside the helix in **2**. Hydrogen atoms of the suc and bipy molecules are omitted for clarity.



(a) (b)

Figure 7. (a) Tetragonal packing of bipy-connected racemic Ni–suc helices (hydrogen atoms and water molecules are omitted for clarity) and (b) the distorted $6^5.8$ network in **2**.

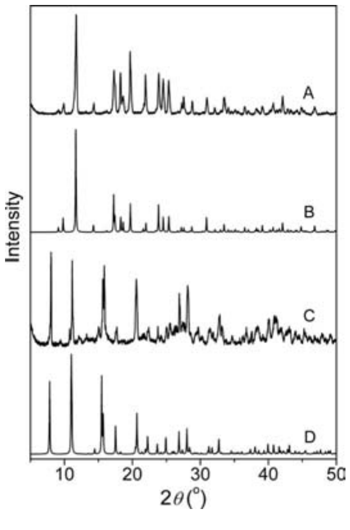


Figure 8. Powder X-ray diffraction patterns of **1** (curve A experimental and curve B simulated) and **2** (curve C experimental and curve D simulated).

nections parallel to the *ab*-plane caused by the fourfold helical nature of the Ni–suc chains.

For both **1** and **2**, the phase purity of the synthesized product was confirmed by comparing the powder X-ray diffraction patterns with those simulated from the single-crystal data using Mercury 2.4 software. The experimental and simulated diffraction patterns are shown in Figure 8. In each case, the very similar experimental and simulated patterns indicate the homogeneous nature of the product.

Conclusions

Two Ni^{II} coordination polymers assembled by *gauche* suc and bipy with the same composition but different degrees of hydration due to their different synthetic reaction conditions have been described. The Ni–suc chains are helical in both complexes, but there is an interesting alteration of the helical axis with the change of hydration. There are homochiral right-handed sixfold helices in dihydrated **1** and both right- and left-handed fourfold helices in monohydrated **2**. Finally, bipy connected helices provide the dense chiral twisting $7^5.9$ and achiral distorted $6^5.8$ networks in **1** and **2**, respectively. The guest water molecules are in the intrahelical channels in **1** and in the interhelical channels in **2**. It is possible that the guest water molecules in the intrahelical channels act as a template and determine the sixfold helical axis of the metal–suc chains and the resulting network topology in **1** and its Cu^{II} and Co^{II} analogues.[23–26] The lack of this template action could be the critical factor for the alteration of the screw axis of the Ni–suc helices in **2** and hence its network topology. We are currently involved in synthesizing coordination polymers of bivalent metal ions with combinations of suc and bipy or similar linear bridging ligands of varying length under various reaction conditions.

Experimental Section

Materials: All chemicals and solvents were available commercially, of analytical grade, and were used without further purification.

Physical Measurements: Microanalytical (C,H,N) data were obtained with a Thermo Finnigan Flash EA1112 elemental analyzer. Netzsch STZ409TC and Mettler Toledo TGA/SDTA instruments were used for TGA. IR spectra were recorded as KBr pellets with a Jasco-5300 FTIR spectrophotometer. A Shimadzu UV-3600 UV/Vis/NIR spectrophotometer was used to record the electronic spectra in the solid state by diffuse reflectance technique using $BaSO_4$ pellets. The CD spectrum of powdered **1** as a KBr pellet was recorded with a Jasco J810 spectropolarimeter. The magnetic susceptibilities at room temperature were measured using a Sherwood Scientific balance. The cryomagnetic measurement with a powdered sample of **1** was performed at a constant magnetic field of 10 kG using the Faraday technique with a set-up comprising a George Associates Lewis coil force magnetometer, a CAHN microbalance, and an Air Products cryostat. $Hg[Co(NCS)_4]$ was used as the standard. Diamagnetic corrections calculated from Pascal's constants,[48] were used to obtain the molar paramagnetic susceptibilities. The X-ray powder diffraction patterns were collected with a Philips PW-3710 diffractometer using Cu-K_α radiation (λ = 1.54184 Å).

Synthesis of $[Ni(suc)(bipy)(H_2O)_2]_n\cdot 2nH_2O$ (1): A dimethylformamide solution (5 mL) of 4,4′-bipyridine (31 mg, 0.2 mmol) was added to an aqueous solution (5 mL) of $Ni(NO_3)_2\cdot 6H_2O$ (58 mg, 0.2 mmol) with stirring at room temperature. After 10 min an aqueous solution (5 mL) of disodium succinate hexahydrate (54 mg, 0.2 mmol) was added slowly with stirring. After 30 min of stirring, the hazy solution was sealed in a glass tube and heated at 120 °C for 3 d followed by slow cooling to room temperature. The light blue needle-shaped crystals were collected by filtration, washed thoroughly with water, and dried in air; yield 60 mg, 74%. $C_{14}H_{20}N_2NiO_8$ (403.03): calcd. C 41.72, H 5.00, N 6.95; found C 41.90, H 4.71, N 6.49. Selected IR (KBr): $\tilde{\nu}$ = 3275 (br), 1611 (m), 1539 (s), 1414 (s), 1225(m), 1065 (m), 812 (s), 636 (m), 467 (m) cm^{-1}. UV/Vis: 1010, 630, 330 (sh), 270 nm.

Synthesis of $[Ni(suc)(bipy)(H_2O)_2]_n\cdot nH_2O$ (2): A dimethylformamide solution (15 mL) of 4,4′-bipyridine (78 mg, 0.5 mmol) was added to an aqueous solution (5 mL) of $Ni(NO_3)_2\cdot 6H_2O$ (140 mg, 0.48 mmol) with stirring at room temperature. After 10 min an aqueous solution (10 mL) of disodium succinate hexahydrate (135 mg, 0.5 mmol) was added slowly with stirring. After 30 min of stirring the mixture was heated in a long narrow necked open glass tube at 80 °C for 3 d and then cooled slowly to room temperature. The blue block-shaped crystals were collected by filtration, washed thoroughly with water, and dried in air; yield 145 mg (75%). $C_{14}H_{18}N_2NiO_7$ (385.01): calcd. C 43.68, H 4.71, N 7.28; found C 43.35, H 4.52, N 6.91. Selected IR (KBr): $\tilde{\nu}$ = 3274 (br), 1613 (m), 1537 (s), 1416 (s), 1217 (m), 1065 (m), 818 (s), 637 (m), 467 cm^{-1} (m) cm^{-1}. UV/Vis: 975, 620, 330 (sh), 275 nm.

X-ray Crystallography: Unit cell parameters and the intensity data for both complexes were obtained at 298 K with a Bruker–Nonius SMART APEX CCD single crystal diffractometer, equipped with a graphite monochromator and a Mo-K_α fine-focus sealed tube (λ = 0.71073 Å) operated at 2.0 kW. In each case, the detector was placed at a distance of 6.0 cm from the crystal. Data were collected with a scan width of 0.3° in ω and an exposure time of 10 s/frame. The SMART software was used for data acquisition and the SAINT-Plus software was used for data extraction.[49] Absorption correction was performed with the SADABS program.[50] Both structures were solved by direct methods and refined on F^2 by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the water molecules were located in the corresponding difference maps and refined with $U_{iso}(H) = 1.5U_{eq}(O)$. The remaining hydrogen atoms were included in the structure factor calculation at idealized positions using a riding model. The SHELX-97 programs[51] available in the WinGx package[52] were used for structure solution and refinement. The ORTEX6a[53] and Platon[54] packages were used for molecular graphics. Significant crystal and refinement data are listed in Table 4.

CCDC-815040 (for **1**) and -815041 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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