

Guest-Inclusion Behavior of Double-Strand 1D Coordination Polymers Based on *N,N'*-Type Schiff Base Ligands

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Four double-strand one-dimensional (1D) coordination polymers, namely, $[\{Ni(N3Py)_2(NO_3)_2\} \cdot (C_6H_6)_x \cdot C_2H_5OH]_n$ (**1**), $[Cd(ImBNN)_2(CH_3C_6H_4SO_3)_2]_n$ (**2**), $[Co(N3OPy)_2(H_2O)_2](ClO_4)_2 \cdot C_6H_6 \cdot H_2O$ (**3**), and $[Co(N3OPy)_2(H_2O)_2](ClO_4)_2 \cdot (C_8H_{10})_x$ (**4**) were obtained from the assembly of three *N,N'*-type Schiff base ligands, 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene (N3Py), 2,5-bis(4'-(imidazol-1-yl)benzyl)-3,4-diaza-2,4-hexadiene (ImBNN), and bis[4-(3-pyridylmethyl-enemino)phenoxy]methane (N3OPy), with transition-metal ions. All complexes were characterized by single-crystal X-

ray diffraction, X-ray powder diffraction, and FTIR measurements. The guest-inclusion behavior of these complexes were investigated by thermogravimetric and X-ray powder diffraction analyses. The structural relationship between the ligands and the cavity sizes and packing fashions have been discussed to elucidate the distinctive guest-inclusion behavior of these complexes.

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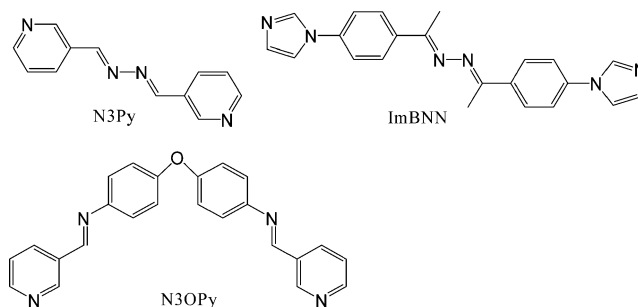
Introduction

In the past decades, porous coordination polymers have attracted much attention of chemists^[1,2] because these polymers are able to host different guests in their cavities and have potential properties in storage and separation.^[3–5] They also find potential applications in the adsorption of small molecules, because the properties of the metal centres and the size and functionality of the bridging organic ligands can be varied.^[6,7] Many factors have been found to influence the network and the topology of coordination polymers, such as the coordination geometry of the metal ions, solvents systems, counter anions, and metal-to-ligand ratios. In principle, selection and synthesis of the organic bridging ligands represents a key step in the design of the architectures of the coordination polymers with specific functionalities. By carefully modifying the size and flexibility of the ligand, numerous 1D, 2D, and 3D supramolecular architectures have been constructed.

One of current endeavors is to synthesize longer organic ligands with the aim to form an assembly of coordination polymers with larger pores. However, the spacious 2D or 3D networks supported by the long spacers normally show

a strong inclination to interpenetrate or polycatenate with each other,^[8] thus achieving close packing to prevent formation of effective channels. On the contrary, the potential porosity that may be provided by 1D coordination polymers has so far drawn little attention, although the 1D structures have been demonstrated to be able to display diverse packing and interweaving modes,^[9] and in some cases, porous frameworks were afforded.^[10] Since the overall frameworks formed by the stacking of 1D polymers are essentially nonrigid in contrast to the 2D and 3D coordination networks, the guest-inclusion behavior of such porous frameworks may have the advantage of showing easy host-guest adaptation and flexible framework shrinkage/extension depending on the guest molecules.

The *N,N'*-type Schiff base ligands have been used widely in the field of supramolecular coordination chemistry, affording a variety of functional 1D to 3D coordination



Scheme 1. Molecular structures of the ligands.

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polymers, many of which are porous and able to host guest molecules.^[11–13] Herein we report four double-strand 1D coordination polymers,^[14] $\{[\text{Ni}(\text{N3Py})_2(\text{NO}_3)_2] \cdot (\text{C}_6\text{H}_6)_x \cdot \text{C}_2\text{H}_5\text{OH}\}_n$ (**1**), $[\text{Cd}(\text{ImBNN})_2 \cdot (\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3)_2]_n$ (**2**), $\{[\text{Co}(\text{N3OPy})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot \text{C}_6\text{H}_6 \cdot \text{H}_2\text{O}\}_n$ (**3**), and $\{[\text{Co}(\text{N3OPy})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot (\text{C}_8\text{H}_{10})_x\}_n$ (**4**), which were constructed from *N,N'*-type Schiff base ligands with different lengths and flexibility, namely, 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene (N3Py), 2,5-bis[4'-(imidazol-1-yl)benzyl]-3,4-diaza-2,4-hexadiene (ImBNN), and bis[4-(3-pyridylmethyleneimino)phenoxy]methane (N3OPy) (Scheme 1).

The different lengths and angles of the ligands lead to the formation of M_2L_2 basic rings with different sizes and guest-inclusion behavior.

Results and Discussion

The ligands N3Py and ImBNN were synthesized following literature methods by reaction of hydrazine with 3-pyridinecarboxaldehyde or 4-(imidazol-1-yl)acetophenone.^[11a,12c] The ligand N3OPy was synthesized by using 4,4'-oxydianiline and 3-pyridinecarboxaldehyde in ethanol in the presence of a few drops of glacial acetic acid.

Table 1. Selected bond lengths [Å] and bond angles [°] for complexes **1–4**.

1 ^[a]			
Ni1–O3	2.080(2)	Ni1–O3(#1)	2.080(2)
Ni1–N1	2.117(3)	Ni1–N1(#1)	2.117(3)
Ni1–N4(#2)	2.145(3)	Ni1–N4(#3)	2.145(3)
O3–Ni1–O3(#1)	180.00(9)	O3–Ni1–N1	94.04(10)
O3(#1)–Ni1–N1	85.96(10)	O3–Ni1–N1(#1)	85.96(10)
O3(#1)–Ni1–N1(#1)	94.04(10)	N1–Ni1–N1(#1)	180.00(11)
O3–Ni1–N4(#2)	93.67(10)	O3(#1)–Ni1–N4(#2)	86.33(10)
N1–Ni1–N4(#2)	93.85(10)	N1(#1)–Ni1–N4(#2)	86.15(10)
O3–Ni1–N4(#3)	86.33(10)	O3(#1)–Ni1–N4(#3)	93.67(10)
N1–Ni1–N4(#3)	86.15(10)	N1(#1)–Ni1–N4(#3)	93.85(10)
N4(#2)–Ni1–N4(#3)	180.00(8)		
2 ^[b]			
Cd1–O3	2.3012(17)	Cd1–O3(#1)	2.3012(17)
Cd1–N4	2.339(2)	Cd1–N4(#1)	2.339(2)
Cd1–N1	2.377(2)	Cd1–N1(#1)	2.377(2)
O3–Cd1–O3(#1)	180.00(1)	O3–Cd1–N4	93.03(7)
O3(#1)–Cd1–N4	86.97(7)	O3–Cd1–N4(#1)	86.97(7)
O3(#1)–Cd1–N4(#1)	93.03(7)	N4–Cd1–N4(#1)	180.0
O3–Cd1–N1	84.32(7)	O3(#1)–Cd1–N1	95.68(7)
N4–Cd1–N1	100.03(8)	N4(#1)–Cd1–N1	79.97(8)
O3–Cd1–N1(#1)	95.68(7)	O3(#1)–Cd1–N1(#1)	84.32(7)
N4–Cd1–N1(#1)	79.97(8)	N4(#1)–Cd1–N1(#1)	100.03(8)
N1–Cd1–N1(#1)	180.0		
3 ^[c]			
Co1–O2(#1)	2.1295(14)	Co1–O2	2.1295(14)
Co1–N4(#2)	2.1825(15)	Co1–N4(#3)	2.1825(15)
Co1–N1	2.1946(15)	Co1–N1(#1)	2.1946(15)
O2(#1)–Co1–O2	180.00(12)	O2(#1)–Co1–N4(#2)	90.52(6)
O2–Co1–N4(#2)	89.48(6)	O2(#1)–Co1–N4(#3)	89.48(6)
O2–Co1–N4(#3)	90.52(6)	N4(#2)–Co1–N4(#3)	180.00(5)
O2(#1)–Co1–N1	91.21(5)	O2–Co1–N1	88.79(5)
N4(#2)–Co1–N1	84.32(6)	N4(#3)–Co1–N1	95.68(6)
O2(#1)–Co1–N1(#1)	88.79(5)	O2–Co1–N1(#1)	91.21(5)
N4(#2)–Co1–N1(#1)	95.68(6)	N4(#3)–Co1–N1(#1)	84.32(6)
N1–Co1–N1(#1)	180.00(11)		
4 ^[d]			
Co1–O2(#1)	2.123(2)	Co1–O2	2.123(2)
Co1–N4(#2)	2.182(2)	Co1–N4(#3)	2.182(2)
Co1–N1	2.193(2)	Co1–N1(#1)	2.193(2)
O2(#1)–Co1–O2	180.00(14)	O2(#1)–Co1–N4(#2)	90.50(9)
O2–Co1–N4(#2)	89.50(9)	O2(#1)–Co1–N4(#3)	89.50(9)
O2–Co1–N4(#3)	90.50(9)	N4(#2)–Co1–N4(#3)	180.00(7)
O2(#1)–Co1–N1	91.16(8)	O2–Co1–N1	88.84(8)
N4(#2)–Co1–N1	84.37(8)	N4(#3)–Co1–N1	95.63(8)
O2(#1)–Co1–N1(#1)	88.84(8)	O2–Co1–N1(#1)	91.16(8)
N4(#2)–Co1–N1(#1)	95.63(8)	N4(#3)–Co1–N1(#1)	84.37(8)
N1–Co1–N1(#1)	180.00(15)		

[a] Symmetry transformations: #1: $-x + 1/2, -y + 1/2, 1 - z$; #2: $x + 1/2, -y + 1/2, z + 1/2$; #3: $-x, y, -z + 1/2$. [b] #1: $-x, -y, -z$. [c] #1: $-x, -y, -z$; #2: $x - 2, y - 1, z - 1$; #3: $2 + x, 1 + y, 1 + z$. [d] #1: $-x, -y, -z$; #2: $x - 2, y - 1, z - 1$; #3: $2 + x, 1 + y, 1 + z$.

Complexes **1**, **2**, **3**, and **4** were prepared by reaction of the corresponding metal salts with the three ligands directly. The metal salts used are: $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cd}(\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3)_2$, and $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. In general, the solution of the metal salt was carefully layered onto the solution of the ligand. The target crystalline complexes formed over a period from 3 d to 2 weeks in various solvent systems, i.e. EtOH/ C_6H_6 for **1**, EtOH/ C_6H_6 /DMF for **2**, EtOH/ C_6H_6 for **3**, and EtOH/ C_8H_{10} for **4**. The presence of ethanol as solvent in **1** and of the anions in **1–4** were confirmed by their characteristic IR absorption bands [3360 cm^{-1} for ethanol; 1384 cm^{-1} and 1314 cm^{-1} for NO_3^- ; 1176 cm^{-1} , 1035 cm^{-1} , and 1011 cm^{-1} for $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$; 1038 cm^{-1} and 1012 cm^{-1} for ClO_4^- in complex **3**; 1102 cm^{-1} for ClO_4^- in complex **4**]. All samples seem to be moisture sensitive and varied amounts of water molecules were adsorbed when the samples were kept in air, which resulted in slightly different compositions to those of the single-crystals, as seen from the elemental analyses results.

Complex **1** was prepared from the rigid, linear ligand N3Py and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. X-ray crystallographic analysis reveals that it is a double-strand 1D chain. The Ni^{II} ion lying on an inversion centre is hexacoordinate with four N-donor atoms from four different N3Py ligands, with N–Ni–N bond angles of $86.15(10)$, $93.67(10)$, and $180.00(11)^\circ$ and Ni–N bond lengths of $2.117(3)$ and $2.145(3)\text{ \AA}$. The two axial positions are occupied by two O-donor atoms from two nitrate ions, with an O–Ni–O bond angle of $180.00(9)^\circ$ and a Ni–O bond length of $2.080(2)\text{ \AA}$ (Table 1). Thus, the central metal ion Ni^{II} adopts an octahedral geometry (Figure 1a). Each N3Py ligand links two metal ions to generate the infinite, double-strand 1D chain containing 22-membered M_2L_2 repeating rings. The $\text{Ni}\cdots\text{Ni}$ distance within the M_2L_2 basic ring is $11.9\text{ \AA}$ and the $\text{N}2\cdots\text{N}3$ distance is $5.3\text{ \AA}$, which define the size of the M_2L_2 ring (Figure 1b).

In complex **1**, no guest molecule is hosted inside the basic M_2L_2 ring. This may be due to the rigidity of the linear ligand and the “V” shape of the M_2L_2 ring, which cannot provide a suitable host environment for the guests. Instead, waving channels are present between adjacent double-strand chains in the *a* direction, in which benzene and ethanol molecules are enclosed (Figure 1c). Therefore, the crystal packing in complex **1** can be regarded to form 2D intercalated layers in the *ac* plane, with alternate stacking of the coordination chains and host molecules along the *b* direction. Guest molecules of benzene and ethanol interact with the double-strand chains through $\pi\cdots\pi$ stacking and C–H $\cdots$ O hydrogen-bonding interactions.

To create a larger M_2L_2 basic ring, the ligand ImBNN was prepared, which is structurally similar to N3Py but longer. Reaction of ImBNN with $\text{Cd}(\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3)_2$ afforded complex **2**. X-ray crystallographic analysis shows that complex **2** has a similar double-strand 1D chain structure. The Cd^{II} ion adopts the same octahedral geometry and is coordinated by four N-donor atoms from four different ImBNN ligands, with N–Cd–N bond angles of $79.97(8)$, $100.03(8)$, and 180° and Cd–N bond lengths of $2.339(2)$ and $2.377(2)\text{ \AA}$. The two axial positions are occu-

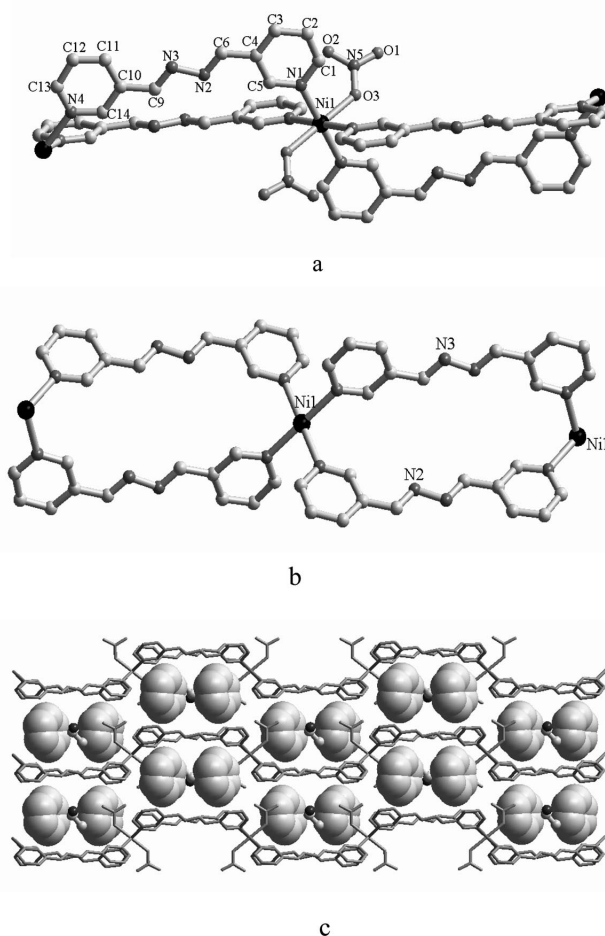


Figure 1. (a) Molecular structure of complex **1** with atomic labeling scheme; (b) M_2L_2 basic rings; (c) guest-filled crystal packing of the 1D chains with a space-fill model for the benzene molecules in complex **1**.

ried by two O-donor atoms from two $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$ ions, with a O–Cd–O bond angle of $180.000(1)^\circ$ and a Cd–O bond length of $2.3012(17)\text{ \AA}$ (Figure 2a). The ImBNN ligands link the metal ions to generate an infinite double-strand 1D chain containing repeating 38-membered M_2L_2 macrocyclic rings with the size of $21.1 \times 4.1\text{ \AA}$, which is defined by the $\text{Cd}\cdots\text{Cd}$ distance versus the $\text{N}3\cdots\text{N}3$ distance within the M_2L_2 basic ring (Figure 2b).

As expected, a much longer M_2L_2 ring was formed in complex **2** than in complex **1**. The length is almost twice as long (21.1 versus $11.9\text{ \AA}$), but the width of the M_2L_2 ring is slightly reduced (4.1 versus $5.3\text{ \AA}$). The two ligands are aligned nearly in a parallel fashion, which prevents accommodation of any guest molecules inside such a compressed long and narrow space. Similar to that in complex **1**, a layered packing fashion is observed in **2**, and apparent channels are formed in the *a* direction because of the weaving arrangement of the 1D chain. However, bulky $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$ anions occupy the channels, which leaves no space to host any guest molecules inside the channel. The adjacent double-strand chains are packed tightly by forming $\pi\cdots\pi$ stacking interactions between the ligands and C–H $\cdots$ O interactions between anions and ligands (Figure 2c).

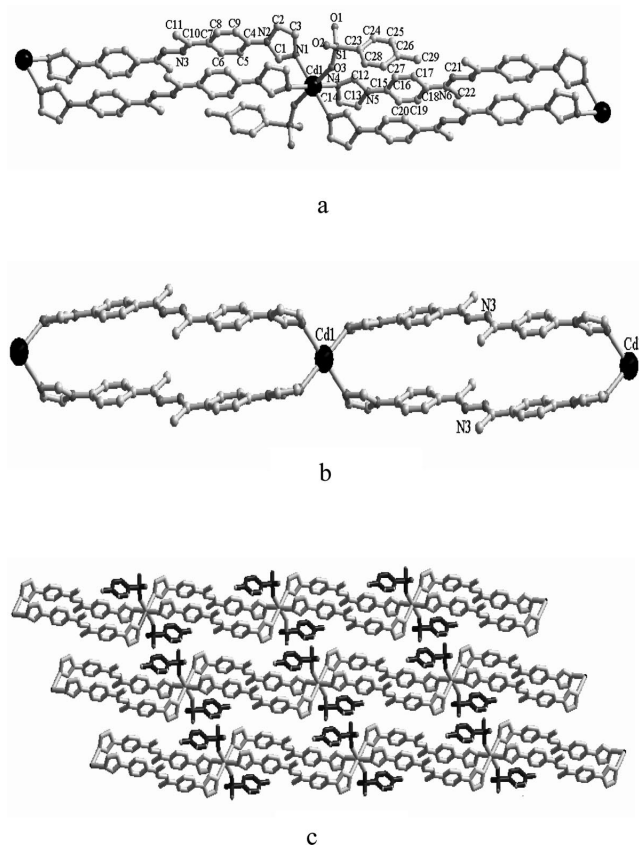


Figure 2. (a) Molecular structure of complex **2** with atomic labeling scheme; (b) M₂L₂ basic rings; (c) crystal packing of the 1D chains in complex **2**.

It is noticeable from complexes **1** and **2** that the rigid ligands are not good candidates for fabrication of double-strand chain structures containing M₂L₂ ring units with effective voids to host guest molecules. To modify the ligand structure, we prepared the long angular ligand N3OPy, which possesses an ether O atom to allow two rigid Schiff base arms to make an angle. Reaction of this ligand with Co(ClO₄)₂·6H₂O gave complex **3**, which shows a similar double-strand 1D structure as in **1** and **2** (Figure 3a). The central Co^{II} ion also adopts an octahedral geometry by binding four N-donor atoms from four N3OPy ligands, with N–Co–N bond angles of 84.32(6), 95.68(6), and 180.00(11)° and Co–N bond lengths of 2.1825(15) and 2.1946(15) Å. The two axial positions are occupied by O-donor atoms from two solvated water molecules, with a O–Co–O bond angle of 180.00(12)° and a Co–O bond length of 2.1295(14) Å.

Since the ligand N3OPy is angular (the ∠C–O–C angle is about 120°), the M₂L₂ basic ring in complex **3** is conformationally distinct from those in complexes **1** and **2**. The four rigid Schiff base arms of the two ligands constitute the four edges and the two Co^{II} ions and two O atoms can be regarded as the vertices. The size of the thus formed rhombic ring is about 20.1 × 12.2 Å, which is estimated by the separation of Co···Co and O1···O1. Therefore, the M₂L₂ ring in **3** is large enough to host a benzene guest as shown

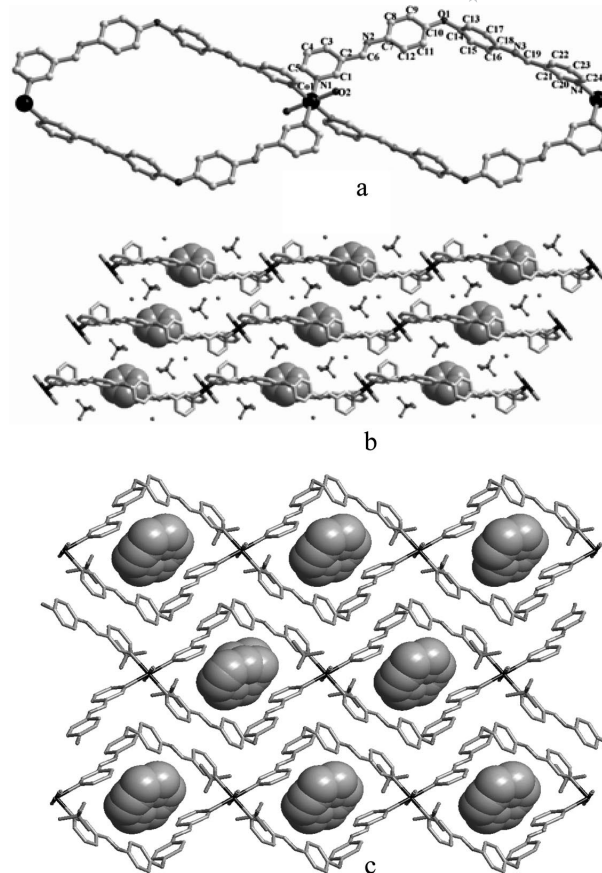


Figure 3. (a) Molecular structures of complexes **3** and **4** with atomic labelling scheme; (b) guest-filled crystal packing of the 1D chains in the *c* direction, showing inclusion of benzene molecules inside the M₂L₂ basic rings in **3**; (c) channels formed in **3** in the *a* direction, in which benzene guest molecules are shown in space-filling mode.

in Figure 3b. The solvated water molecules and ClO₄[−] anions are located between the double-strand chains, and $\pi \cdots \pi$ stacking between the ligands and C–H···O hydrogen bonds between ClO₄[−] or water and the ligands are formed. The double-strand chains can be considered to align parallelly in the *bc* direction to form layers as depicted in Figure 3c. Channels are formed in the *a* direction, in which benzene guest molecules are accommodated. Such a channel, which has a layered packing fashion, is apparently different from those in complexes **1** and **2**, which show intercalation of the guest in between the coordination layers.

Complex **4** has actually an analogous structure to that of **3** as they have the same coordination framework and similar M₂L₂ basic rings with the size of about 20.1 × 12.1 Å, as shown in Figure 4. Instead of the benzene molecules, *m*-xylene guest molecules are located within the M₂L₂ basic rings, which form the same channels in the *a* direction in the crystal lattice. This finding indicates that the [Co(N₃OPy)₂(H₂O)₂]²⁺ coordination framework in both **3** and **4** can provide robust cavities to accommodate guest molecules with similar polarity and structural natures.

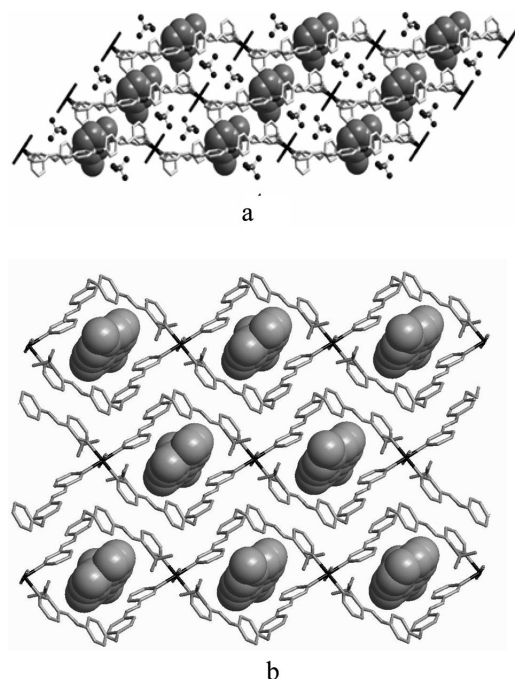


Figure 4. (a) Guest-filled crystal packing of the 1D chains in the *c* direction, showing inclusion of *m*-xylene molecules inside the M_2L_2 basic rings in **4**; (b) Channels formed in **4** in the *a* direction, where *m*-xylene guest molecules are shown in space-filling mode.

Guest Inclusion Behavior

As discussed above, X-ray single-crystal diffraction analysis indicates that complex **2** contains no solvated molecules. However, thermogravimetric analyses (TGA) of complex **2** gives a curve showing a small gradual weight loss, which suggests that the sample is moisture sensitive (Figure 5). The coordination framework of complex **2** collapses in the temperature range 300–660 °C. X-ray powder diffraction (XRD) analysis of the bulk sample shows a pattern that closely matches the simulated one, which is indicative of the pure solid-state phase (Figure 6).

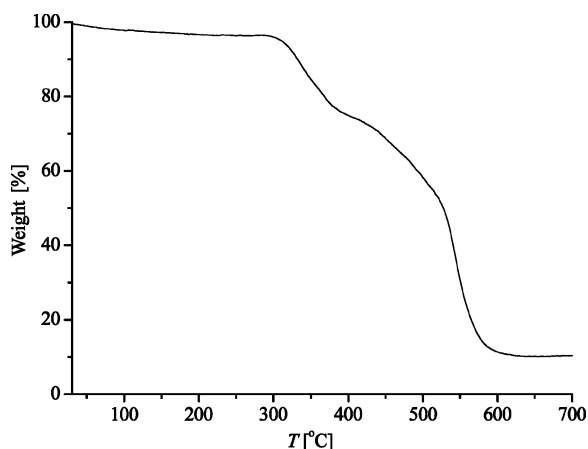


Figure 5. TG curve for complex **2**.

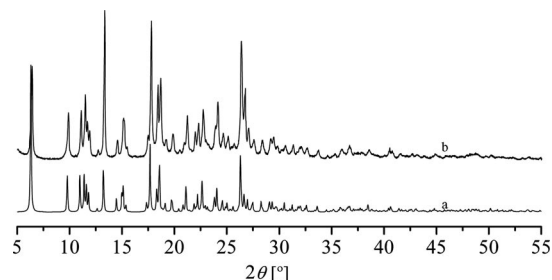


Figure 6. X-ray powder diffraction patterns of complex **2**: (a) simulated and (b) measured.

To study the guest-inclusion behavior of the guest-containing complexes **1**, **3**, and **4**, TGA and XRD measurements were performed separately for the as-prepared samples, solvent-free samples obtained upon heating at certain temperatures, and samples after readsorbing guest molecules.

The TG curve of the fresh sample of complex **1** shows a weight loss of 25.7% in the temperature range 20–195 °C, which corresponds to the loss of one ethanol molecule and two benzene molecules per formula unit (calculated 25.1%). The coordination framework of complex **1** collapses in the range 190–420 °C (Figure 7a). The solvent-free sample $[Ni(N3Py)_2(NO_3)_2]_n$ (denoted as complex **1'**) was obtained by heating a crystalline sample of complex **1** to 100 °C for 5 h in air. The TG analysis of **1'** shows no weight loss before 200 °C, which indicates that all guest molecules had evaporated. A similar weight loss pattern was observed from 200–420 °C as in **1**, which indicates the decomposition of the coordination framework (Figure 7b). By dipping solvent-free sample **1'** in benzene for 2 d, complex **1''** was obtained. The TG analysis of **1''** shows a weight loss of 10.8% in the temperature range 30–220 °C, which corresponds to the loss of approximately one benzene molecule per formula unit (expected 11.4%) [Figure 7c]. This finding suggests that the “dry” complex **1'** can readsorb about one benzene molecule

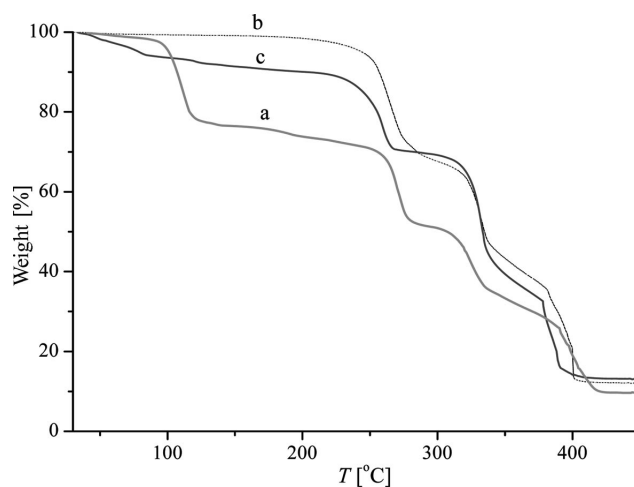


Figure 7. TG curves for the complexes: (a) as-prepared $[Ni(N3Py)_2(NO_3)_2] \cdot (C_6H_6)_2 \cdot C_2H_5OH$ (**1**); (b) solvent-free $[Ni(N3Py)_2(NO_3)_2]_n$ (**1'**); (c) after the guest molecule is readsorbed, $[Ni(N3Py)_2(NO_3)_2] \cdot C_6H_6$ (**1''**).

to give a complex **1''** with the formula $[\text{Ni}(\text{N3Py})_2(\text{NO}_3)_2] \cdot \text{C}_6\text{H}_6$, but is not able to revert to complex **1** completely.

It was found that fresh crystals of complex **1** lose their transparency quickly after leaving the mother liquid. This means that the solvated molecules may escape partially in air, which usually causes changes in the crystal structure. Indeed, the XRD measurement of the opaque sample reveals significant variations in the intensity of some peaks (Figure 8b) relative to the pattern simulated from the single-crystal diffraction data (Figure 8a). After all guest molecules from the crystals are released by heating, the XRD analysis was performed for complex **1'**. As shown in Figure 8c, the resulting pattern exhibits new distinctive features, which may suggest further structural transformation. The XRD pattern of the readsorbed sample **1''** (Figure 8d) resembles that of **1'**, but a few peaks are shifted in position and vary in intensity.

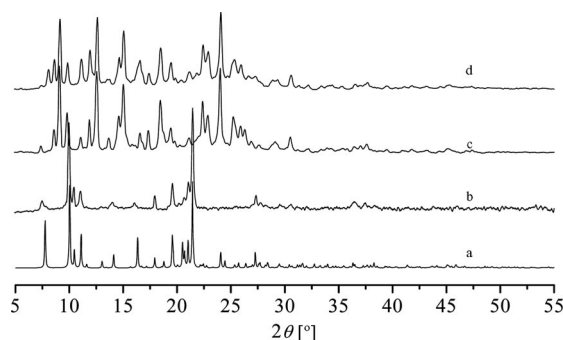


Figure 8. (a) Simulated X-ray powder diffraction pattern of complex **1**. Measured X-ray powder diffraction patterns: (b) as-prepared sample of complex **1**; (c) solvent-free complex **1'**; (d) after the guest molecule is readsorbed, complex **1''**.

The above observations indicate that the crystal structure of complex **1** is subject to subtle changes in the solvated molecules. As the guest molecules leave and re-enter, crystal-to-crystal phase transformation occurs. This is expected because complex **1** has intercalated packing layers in the crystal lattice. Movement of the solvent may easily trigger sliding of the double-strand chain layers, which will result in alteration of the unit cell parameters. However, since the overall coordination framework has a relatively high thermostability (around 200 °C), desorption and readsorption of guest molecules only leads to crystal-to-crystal phase change without collapse of the crystal lattice completely. Readsorption of the guest molecules is obviously not complete, and the solid-state phase change is not reversible.

The TG curve for complex **3** shows a weight loss of 8.0% in the temperature range 30–200 °C, which corresponds to the loss of one water molecule and one benzene molecule (calculated 8.4%) per formula unit. This suggests evaporation of all solvent molecules. The coordination framework collapses in the range 280–600 °C (Figure 9a). Complex **3'** was obtained after heating the crystalline sample of complex **3** to 100 °C for 5 h in air. The TG analysis confirms that there is no weight loss before 250 °C, which indicates that there are no benzene and water molecules retained in **3'**. The coordination framework of **3'** collapses in the range

250–600 °C (Figure 9b), and this is consistent with the collapse of the guest-inclusion sample. After sample of **3'** was dipped in benzene for 2 d, complex **3''** was obtained. The TG analysis shows a weight loss of 12.8% in the temperature range 30–250 °C, which corresponds to the loss of two benzene molecules per formula unit (expected 12.9%, Figure 9c). This means that the guest-free complex **3'** can readsorb twice the number of benzene guest molecules than those contained in complex **3**. In the temperature range 300–600 °C, the decomposition behavior of the coordination framework of the sample in which the guest molecules are readsorbed remains rather similar to that of complex **3**.

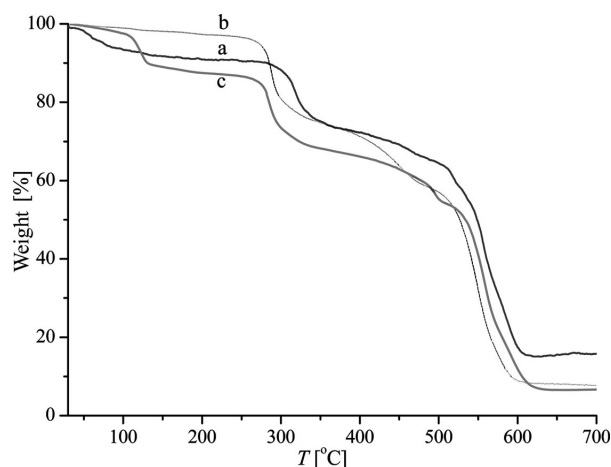


Figure 9. TG curves for the complexes: (a) as-prepared $[\text{Co}(\text{N3OPy})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot \text{C}_6\text{H}_6 \cdot \text{H}_2\text{O}$ (**3**); (b) solvent-free $[\text{Co}(\text{N3OPy})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (**3'**); (c) after the guest molecules are readsorbed, $[\text{Co}(\text{N3OPy})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot (\text{C}_6\text{H}_6)_2$ (**3''**).

The single crystals of complex **3** rapidly crack when exposed to air, which is indicative of the partial escape of the guest molecules from the crystal lattice. The XRD pattern of such a sample displays small shift in the position of some of the peaks relative to those in the simulated pattern of the single crystal (Figure 10a and 10b). When all the solvated molecules are completely removed by heating, the XRD pattern of the solvent-free complex **3'** maintains the main profile of the guest-inclusion complex **3**. However, a few new peaks appear, and the intensity of some of the peaks alters (Figure 10c). After readsorption of benzene guest molecules, complex **3''** gives rise to an XRD pattern that resembles the simulated pattern (Figure 10d). These findings suggest that the crystal packing in complex **3** is more tolerant towards the desorption and re-adsorption of guest molecules than that in complex **1**. From the structural analysis, we can see that, in contrast to complex **1**, the layered packing in complex **3** is independent of the type of guest molecules. The guest molecules can move along the channels that are formed by the M_2L_2 rings within the double-strand 1D chains. Therefore, the desorption and re-adsorption of guest molecules is not expected to show a significant influence on the overall crystal lattice. The XRD results indicate that slight crystal-to-crystal phase transformation occurs during the movement of the guest molecules; however, the crystal framework is almost restored after de-

sorbing and then readsorbing of the guest molecules, even after twice the amount of the benzene guest molecules is readsorbed. This confirms the permanence of the porous framework in complex **3**, which is in agreement with the TGA results and the structural analysis.

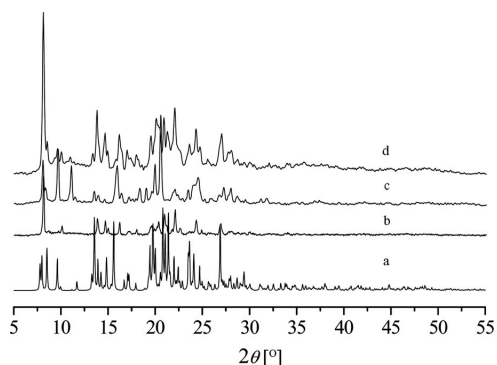


Figure 10. (a) Simulated X-ray powder diffraction pattern of complex **3**. Measured X-ray powder diffraction patterns: (b) as-prepared sample of complex **3**; (c) solvent-free complex **3'**; (d) after the guest molecules are readsorbed, complex **3''**.

The TG curve of complex **4** shows a weight loss of 9.9% in the temperature range 30–160 °C, which can be assigned to the loss of one *m*-xylene molecule per formula unit (calculated 9.2%). In addition, a small weight loss of about 3.3% in the temperature range 160–205 °C appears. This may be attributed to the loss of two coordination water molecules (calculated 3.1%), followed by complete collapse of the coordination framework from 270 to 650 °C (Figure 11a). The solvent-free complex **4'** was obtained by heating a crystalline sample of complex **4** to 150 °C for 15 h in air. The TG analysis shows no weight loss before 160 °C, which suggests that there is no remaining *m*-xylene molecule in **4'**. From 160 to 600 °C, the sample **4'** displays a similar coordination-framework decomposition process to that of the guest-inclusion complex **4** (Figure 11b). After **4'** was dipped in *m*-xylene for 2 d, complex **4''** was obtained. The TG analysis shows a gradual weight loss of 9.6% in the temperature range 30–180 °C, which corresponds to the loss of one *m*-xylene molecule per formula unit (expected 9.2%). Thereafter, the coordination framework decomposes in a similar way to that of complex **4**, although the final temperature is lower, before 550 °C (Figure 11c). These results indicate that the guest molecules in complex **4** can be removed and readsorbed, but *m*-xylene guest molecules cannot be readsorbed as much as the guest molecules in **3**. The host framework displays a more complicated interaction with the guest molecules relative to that in complex **3**. This means that the absence of guest water molecules and the slightly different molecular structure of *m*-xylene guest molecules in complex **4** may impart a delicate influence on the guest-inclusion behavior relative to that of complex **3**.

The solid-state phase information during the desorption and readsorption of the guest molecules has been checked by XRD measurements. The as-prepared sample of complex **4** exhibits an XRD pattern that closely matches the simulated pattern from the single-crystal analysis (Fig-

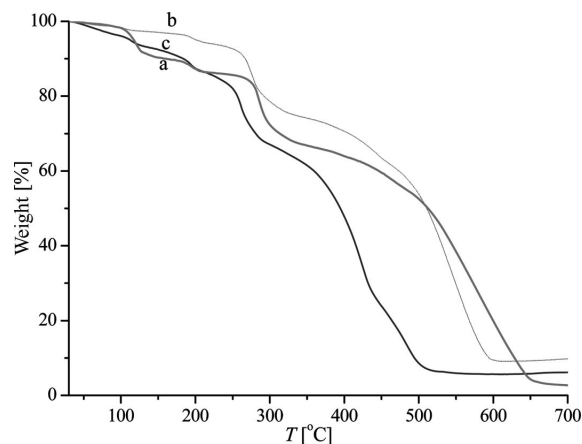


Figure 11. TG curves for the complexes: (a) as-prepared $\{[\text{Co}(\text{N3OPy})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot \text{C}_8\text{H}_{10}\}_n$ (**4**); (b) solvent-free $\{[\text{Co}(\text{N3OPy})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2\}_n$ (**4'**); (c) after the guest molecule is readsorbed, $\{[\text{Co}(\text{N3OPy})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot \text{C}_8\text{H}_{10}\}_n$ (**4''**).

ure 12a and 12b). The XRD pattern of the solvent-free complex **4'** is slightly different with the appearance of a few small peaks (Figure 12c). After readsorption of the guest molecule, the XRD pattern of complex **4''** retains the major pattern profile of that of complex **4**, but complex **4** does not seem to be recovered completely (Figure 12d). These observations suggest that a fine crystal-to-crystal phase change accompanies the desorption and readsorption process of the guest molecules; however, the main crystal framework is well supported by the layered 1D coordination polymers. The channels formed by the double-strand chains allow the movement of larger guest molecules (*m*-xylene in **4** versus benzene in **3**), but may have more interactions with the guests.

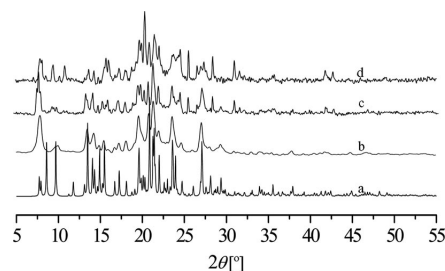


Figure 12. (a) Simulated X-ray powder diffraction pattern of complex **4**. Measured X-ray powder diffraction patterns: (b) as-prepared sample of complex **4**; (c) solvent-free complex **4'**; (d) after the guest molecule is readsorbed complex **4''**.

Conclusions

Four double-strand 1D coordination polymers were prepared by using three Schiff base *N,N'*-type ligands, N3Py, ImBNN, and N3OPy, with varied spacer lengths and structural flexibility. The single-crystal structural analyses indicate that the size and shape of the common M_2L_2 basic rings in these complexes are different because of the different nature of the ligands. In complexes **1** and **2**, the M_2L_2

rings do not afford effective voids to accommodate the guest molecules because of the linear rigidity of the N3Py and ImBNN ligands. An intercalated layering crystal packing fashion is observed in complexes **1** and **2**; complex **1** hosts guest molecules in between the adjacent double-strand 1D chains, while complex **2** contains bulky counteranions that occupy the apparent channels. Larger M_2L_2 rings are formed by using the long angular N3OPy ligand in complexes **3** and **4**, which afford spacious voids to host benzene or *m*-xylene guest molecules. In addition, these M_2L_2 rings constitute a 1D channel through parallel alignment of the double-strand chains in the crystal lattice in **3** and **4**. This results in permanent porosity after removal of the guest molecules. The study of the guest-inclusion behavior of complexes **1**, **3**, and **4** indicates that crystal-to-crystal phase transformation is accompanied with desorption and readsorption of the guest molecules. A significant solid-state phase change is observed in complex **1** during the movement of the guest molecule, which is inherent to its intercalated layering packing fashion. On the contrary, complexes **3** and **4** have more robust porous frameworks, which facilitate complete guest desorption and readsorption. However, although the complexes **3** and **4** contain the same host frameworks, they display adaptive guest-inclusion behavior towards different guest molecules. For complex **3**, twice the amount of benzene guest molecules can be readsorbed by the guest-free complex without remarkable change of the crystal framework, while for complex **4**, the *m*-xylene guest molecules noticeably interact with the host framework and the same amount of guest molecules are readsorbed after removal.

Experimental Section

Materials and Methods: All starting materials and solvents were obtained from commercial sources and used without further purification. The ligands N3Py and ImBNN were synthesized following literature methods.^[11a,12c] Infrared spectra were measured on a Nicolet/Nexus-670 FTIR spectrometer with KBr pellets. X-ray powder diffraction data was recorded on a Bruker D8 Advance diffractometer at 40 kV, 40 mA with a Cu-target tube and a graphite monochromator. Thermogravimetric analysis (TGA) was performed in air and under 1 atm. of pressure at a heating rate of 10 °C/min on a NETZSCH Thermo Microbalance TG 209 F3 Tarsus.

Syntheses

N3OPy: 4,4'-Oxydianiline (2 g, 10 mmol) and 3-pyridinecarboxaldehyde (1.95 mL, 20 mmol) were mixed in ethanol (80 mL). After addition of eight drops of glacial acetic acid, the mixture was heated at reflux for 24 h. The solution was slowly evaporated to near dryness under reduced pressure, and subsequently cooled to room temperature, after which a white precipitate was obtained. After recrystallization from hot ethanol, the white product was harvested. Yield: 2.70 g (71 %). ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 9.01 (s, 2 H, Py-H), 8.69–8.71 (d, ³*J* = 4.5 Hz, 2 H, Py-H), 7.41–7.45 (dd, ³*J* = 4.8, ³*J* = 7.8 Hz, 2 H, Py-H), 8.29–8.31 (d, ³*J* = 7.8 Hz, 2 H, Py-H), 8.54 (s, 2 H, –CH=N), 7.26–7.29 (d, ³*J* = 8.7 Hz, 4 H, Ph-H), 7.06–7.09 (d, ³*J* = 8.7 Hz, 4 H, Ph-H) ppm. IR (KBr): $\tilde{\nu}$ = 3056 (m), 2880 (m), 1622 (s), 1588 (s), 1496 (s), 1419

(s), 1326 (s), 1283 (s), 1186 (s), 1102 (s), 977 (m), 845 (s), 700.89 (s), 541 (s) cm^{−1}. C₂₄H₁₈N₄O (378.4): calcd. C 76.16, H 4.80, N 14.81; found C 76.41, H 4.90, N 14.62.

{[Ni(N3Py)₂(NO₃)₂](C₆H₆)_x·C₂H₅OH]_n (1): Ni(NO₃)₂·6H₂O (29 mg, 0.10 mmol) was dissolved in ethanol (3 mL) and then carefully layered onto a solution of N3Py (42 mg, 0.20 mmol) in C₆H₆ (4 mL). After three days, green block crystals suitable for single-crystal X-ray analysis formed at the interface of the two solutions. Yield 48 mg (60%) based on the ligand. IR (KBr): $\tilde{\nu}$ = 3360 (m), 1630 (s), 1607 (w), 1415 (m), 1384 (s), 1314 (m), 1192 (w), 1106 (w), 1035 (w), 973 (w), 956 (w), 878 (w), 821 (w), 704 (m), 687 (m), 645 (w), 420 (w) cm^{−1}. C₃₂H₃₆N₁₀NiO₉ (1·2H₂O, *x* = 1, 763.38): calcd. C 50.35, H 4.75, N 18.35; found C 50.42, H 4.45, N 18.74.

[Cd(ImBNN)₂(CH₃C₆H₄SO₃)₂]_n (2): Cd(CH₃C₆H₄SO₃)₂ (23 mg, 0.05 mmol) was dissolved in ethanol (3 mL) and then carefully layered onto a solution of ImBNN (19 mg, 0.05 mmol) in C₆H₆ and DMF (2:1, 3 mL). After about two weeks, yellow block crystals suitable for single-crystal X-ray analysis formed at the interface of the two solutions. Yield 15 mg (50%) based on the ligand. IR (KBr): $\tilde{\nu}$ = 3123 (m), 1604 (s), 1520 (s), 1488 (m), 1362 (m), 1306 (m), 1247 (s), 1176 (s), 1120 (s), 1060 (m), 1035 (m), 1011 (m), 962 (w), 921 (w), 830 (s), 752 (w), 681 (m), 568 (m) cm^{−1}. Cd_{0.5}C₂₉H₂₇N₆O₃S (595.83): calcd. C 58.46, H 4.57, N 14.10; found C 58.30, H 4.62, N 13.90.

{[Co(N3OPy)₂(H₂O)₂](ClO₄)₂·C₆H₆·H₂O]_n (3): Co(ClO₄)₂·6H₂O (19 mg, 0.05 mmol) was dissolved in ethanol (3 mL) and then carefully layered onto a solution of N3OPy (38 mg, 0.10 mmol) in C₆H₆ (8 mL). After about two weeks, brown block crystals suitable for single-crystal X-ray analysis formed at the interface of the two solutions. Yield 17 mg (30%) based on the ligand. IR (KBr): $\tilde{\nu}$ = 3421 (m), 1626 (s), 1494 (s), 1429 (w), 1239 (s), 1120 (s), 837 (m), 703 (m), 625 (m), 419 (w) cm^{−1}. C₅₄H₅₀Cl₂CoN₈O₁₄ (3·H₂O, 1164.86): calcd. C 55.68, H 4.33, N 9.62; found C 55.64, H 4.03, N 9.70.

{[Co(N3OPy)₂(H₂O)₂](ClO₄)₂·(C₈H₁₀)_x]_n (4): Co(ClO₄)₂·6H₂O (19 mg, 0.05 mmol) was dissolved in ethanol (3 mL) and then carefully layered onto a solution of N3OPy (38 mg, 0.10 mmol) in *m*-xylene (8 mL). After about two weeks, brown block crystals suitable for single-crystal X-ray analysis formed at the interface of the two solutions. Yield 17 mg (30%) based on the ligand. IR (KBr): $\tilde{\nu}$ = 3415 (s), 1627 (m), 1494 (s), 1426 (m), 1329 (w), 1284 (w), 1238 (s), 1202 (m), 1102 (s), 8407 (m), 704 (m), 624 (m), 545 (w) cm^{−1}. C₅₂H₄₉Cl₂CoN₈O₁₄ (4·2H₂O, *x* = 0.5, 1158.26): calcd. C 54.79, H 4.33, N 9.83; found C 55.11, H 4.37, N 9.51.

X-ray Structure Analyses: The intensity data of complex **1** was collected on an Enraf Nonius CAD4 four-cycle diffractometer (Mo-*K*_α radiation, λ = 0.71073 Å) equipped with a graphite crystal monochromator situated in the incident beam. The unit cell parameters were determined by least-squares refinement by using the setting 2 θ angles of 25 carefully centered reflections. The reflections of complex **2** were collected on an Oxford Gemini S Ultra diffractometer and those of complexes **3** and **4** were collected on a Bruker Smart 1000 CCD diffractometer equipped with graphite monochromated Mo-*K*_α radiation (λ = 0.71073 Å). The structures were solved by direct methods followed by difference Fourier syntheses and refined by the full-matrix least-squares method against *F*_o² with the SHELXTL software.^[15] The coordinates of the non-hydrogen atoms were refined anisotropically except for those explained below. All hydrogen atoms were introduced in calculated positions. In complex **1**, the solvated ethanol molecules are disordered over two positions. The solvated water molecule in complex **3** is distributed over two sites, which were assigned half occupancy without addition of the hydrogen atoms. The benzene molecules

Table 2. Crystallographic data for complexes 1–4.

	1	2	3	4
Empirical formula	C ₃₈ H ₃₈ N ₁₀ NiO ₇	C ₂₉ H ₂₇ Cd _{0.5} N ₆ O ₃ S	C ₅₄ H ₄₈ Cl ₂ CoN ₈ O ₁₃	C ₅₆ H ₅ ·Cl ₂ CoN ₈ O ₁₂
Formula weight	805.49	595.83	1146.83	1156.87
Crystal system	monoclinic	triclinic	triclinic	triclinic
Space group	C2/c	P1	P1	P1
a [Å]	10.772(2)	9.8714(13)	9.9034(11)	9.8175(11)
b [Å]	16.887(3)	9.9271(19)	12.5021(14)	12.4818(14)
c [Å]	23.130(5)	14.797(3)	12.8784(15)	12.8567(14)
α [°]	90	87.270(16)	112.282(2)	111.215(2)
β [°]	99.98(3)	71.388(15)	109.017(2)	109.160(2)
γ [°]	90	74.944(14)	92.466(2)	92.401(2)
V [Å ³]	4143.8(14)	1326.0(4)	1369.4(3)	1364.0(3)
Crystal dimensions [mm]	0.60 × 0.40 × 0.30	0.40 × 0.35 × 0.30	0.45 × 0.39 × 0.30	0.32 × 0.25 × 0.12
Z	4	2	1	1
ρ _{calcd.} [g cm ^{−3}]	1.291	1.492	1.391	1.408
μ [mm ^{−1}]	0.526	0.556	0.482	0.483
T [K]	293(2)	150(2)	150(2)	150(2)
R(int)	0.0174	0.0287	0.0211	0.0155
R ₁ [I > 2σ(I)]	0.0537	0.0367	0.0546	0.0535
wR ₂ [I > 2σ(I)]	0.1359	0.1018	0.1573	0.1498
S	1.038	1.030	1.073	1.037

show severe disorder in two adjacent positions and were modeled by the AFIX 66 restraint in the refinement. In complex **4**, the *m*-xylene guest molecules are also badly disordered over two positions. The same model was applied as in complex **3**, and all carbon atoms were refined isotropically. Crystallographic data and other pertinent information for complexes **1–4** are summarized in Table 2. CCDC-660473, -660474, -660475 and -660476 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.

Acknowledgments

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