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Synthesis and structure of two new coordination polymers featuring noncentrosymmetric inclusion of hydrogen-bonded species

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Abstract

Two new noncentrosymmetric coordination polymers, $[(\text{H}_2\text{O})_2\text{Co}(\text{BPY})(\text{BPEN})_2] \cdot (\text{BPEN})_{1.6} \cdot (\text{BPY})_{0.4} \cdot 2\text{NO}_3 \cdot 4.65\text{H}_2\text{O}$ and $[(\text{H}_2\text{O})_2\text{Ni}(\text{BPY})(\text{BPEN})_2] \cdot (\text{BPEN})_{1.6} \cdot (\text{BPY})_{0.4} \cdot 2\text{NO}_3 \cdot 4.65\text{H}_2\text{O}$, have been synthesized under hydrothermal conditions. The structure consists of large rectangular grid networks. The acentricities of the compounds were introduced by unbalanced inclusion species. Both 4,4'-bipyridine (BPY) and 1,2-bis(4-pyridyl)ethylene (BPEN) display pure covalent, hydrogen and bifunctional bonding modes in the structure.

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Keywords: Coordination polymer; Noncentrosymmetric structures; Metal–organic framework; Inclusion compounds; Rectangular grid; Bifunctional ligand

1. Introduction

Design and synthesis of metal–organic coordination polymers based upon the concept of crystal engineering has been attracting attention in supramolecular chemistry and metal–organic coordination polymers. The intense research activities have recently produced many new metal–organic polymers with great diversity [1–6]. The rational approach to synthesizing desirable materials such as noncentrosymmetric polymers with guest-trapping capabilities, however, remains elusive [7]. Unexpected novel compounds are sometimes obtained [8]. We have recently demonstrated a new approach to control the dimensionality of mixed-ligand framework coordination polymers by utilizing pure covalent bonding interactions under hydrothermal conditions [9] and the construction of a three-dimensional (3-D) structure based upon a two-dimensional (2-D) network linked by hydrogen bonds [10]. The utilization of hydrogen bonds

is a well-known design principle in the construction of supramolecular architecture and crystal engineering [11–13]. Although 4,4'-bipyridine (BPY) and 1,2-bis(4-pyridyl)ethylene (BPEN) are well known as rigid linear building blocks favoring covalent bonding, their bifunctional capability is also very interesting. Bi-functional ligands adopt advantages from both sturdy covalent bonding and flexible non-covalent bonding interactions, which represent a unique feature for their solubility and flexible properties that differ from zeolites as functional materials. Soluble metal–organic complexes with hydrogen-bonding capabilities are very useful in generating metal–organic nanofibers [14] and as chemotherapeutic reagents [15]. Our recent success in using mixed-ligand building blocks has prompted us to test the strategy for the rational approach to noncentrosymmetric materials with guest-trapping capabilities by synthesizing the two new mixed-ligand and mixed-bonding metal–organic polymers, $[(\text{H}_2\text{O})_2\text{Co}(\text{BPY})(\text{BPEN})_2] \cdot (\text{BPEN})_{1.6} \cdot (\text{BPY})_{0.4} \cdot 2\text{NO}_3 \cdot 4.65\text{H}_2\text{O}$ (1) and $[(\text{H}_2\text{O})_2\text{Ni}(\text{BPY})(\text{BPEN})_2] \cdot (\text{BPEN})_{1.6} \cdot (\text{BPY})_{0.4} \cdot 2\text{NO}_3 \cdot 4.65\text{H}_2\text{O}$ (2), with noncentrosymmetric inclusion of guest species in the rectangular grid framework structures.

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2. Experimental

2.1. Materials and methods

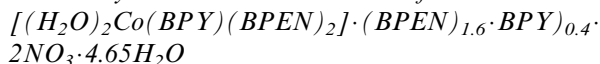
All chemicals were purchased from Aldrich and used without further purification. Thermal gravimetric analysis and differential thermal analysis were performed on a TGA 2050 Thermal Gravimetric Analyzer with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$.

2.2. Synthesis

Both compounds **1** and **2** were synthesized by reacting $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.1455 g) or $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.1455 g) with BPY (0.0781 g) and BPEN (0.1842 g) in the mole ratio of 1:1:2 in 6 ml water. The reactions were carried out in a 23-ml acid digestion bomb at $120\text{ }^{\circ}\text{C}$ for 3 days. The products, orange crystals of **1** and green crystals of **2**, were washed with water and acetone and dried in air. The yield is 68% for **1** and 73% for **2**, respectively.

3. Single-crystal structure determination

3.1. X-ray structure determination of



All measurements were made with a Siemens SMART platform diffractometer equipped with a 1K CCD area detector. A hemisphere of data (1271 frames at 5 cm

detector distance) was collected using a narrow-frame method with scan widths of 0.30° in omega and an exposure time of 30 s. The first 50 frames were re-measured at the end of data collection to monitor instrument and crystal stability, and the maximum correction on I was $<1\%$. The data were integrated using the Siemens SAINT program, with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. A psi scan absorption correction was applied based on the entire data set. Redundant reflections were averaged. Final cell constants were refined using 6590 reflections having $I > 10\sigma(I)$, and these, along with other information pertinent to data collection and refinement, are listed in Table 1. The Laue symmetry was determined to be $2/m$, and from the systematic absences noted the space group was shown to be either Cc or $C2/c$. Although the main polymeric framework fits well on a twofold axis, the remaining anions and solvents do not conform to this symmetry and necessitate refinement in the lower symmetry space group Cc . Large correlations were noted between corresponding variables within the main polymeric chain, and eventually variable distance constraints had to be employed. While this strong pseudo-symmetry might seem to indicate that $C2/c$ is the correct space group, careful consideration shows this to be impossible. There are only four metal atoms in the unit cell, and since space group $C2/c$ has 8 equiv. positions the metal would have to reside on a special position in this case. As shown clearly in Fig. 1, the

Table 1
Crystallographic data and refinement details for **1** and **2**

Complex	1	2
Formula	$[(\text{H}_2\text{O})_2\text{Co}(\text{N}_2\text{C}_{10}\text{H}_8)(\text{N}_2\text{C}_{12}\text{H}_{10})_2] \cdot 1.6(\text{N}_2\text{C}_{12}\text{H}_{10}) \cdot 0.4(\text{N}_2\text{C}_{10}\text{H}_8) \cdot 2\text{NO}_3 \cdot 4.65\text{H}_2\text{O}$	$[(\text{H}_2\text{O})_2\text{Ni}(\text{N}_2\text{C}_{10}\text{H}_8)(\text{N}_2\text{C}_{12}\text{H}_{10})_2] \cdot 1.6(\text{N}_2\text{C}_{12}\text{H}_{10}) \cdot 0.4(\text{N}_2\text{C}_{10}\text{H}_8) \cdot 2\text{NO}_3 \cdot 4.65\text{H}_2\text{O}$
M	1177.41	1177.19
Temperature (K)	223(2)	223(2)
Wavelength (\AA)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	Cc	Cc
a (\AA)	17.961(1)	18.019(1)
b (\AA)	11.451(1)	11.357(1)
c (\AA)	28.537(1)	28.461(1)
β ($^{\circ}$)	98.397(1)	98.183(1)
V (\AA^3)	5806.5(5)	5765.1(5)
Z	4	4
ρ_{calc} (g cm^{-3})	1.347	1.356
μ (mm^{-1})	0.369	0.410
Crystal size (mm)	$0.30 \times 0.25 \times 0.15$	$0.40 \times 0.20 \times 0.12$
Collected θ range	2.12–22.53	1.45–22.52
Index ranges	$-18 \leq h \leq 19, 0 \leq k \leq 12, -30 \leq l \leq 30$	$-19 \leq h \leq 18, 0 \leq k \leq 12, -29 \leq l \leq 30$
Reflections collected	12 321	12 195
Independent reflections	7024 ($R_{\text{int}} = 0.0257$)	6824 ($R_{\text{int}} = 0.0232$)
Goodness-of-fit F^2	1.032	1.052
R [$I > 4\sigma(I)$]	0.0372	0.0334
R_w [$I > 4\sigma(I)$]	0.0936	0.0840

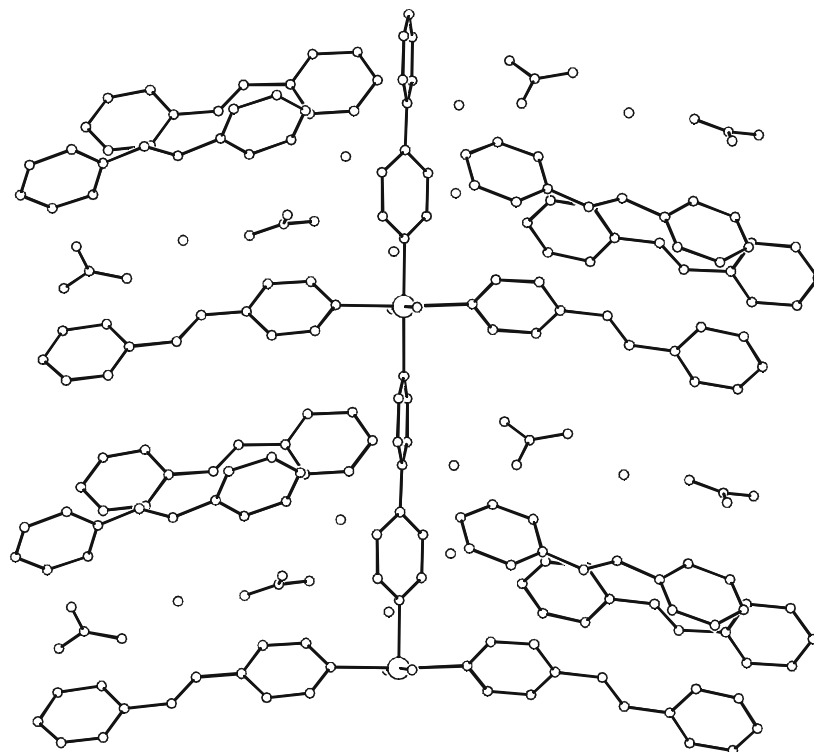


Fig. 1. View of the polymeric chain along *b*, including anions and solvents. The breaking of the twofold symmetry of the core polymer by the interstitial material is clear. Only one orientation of each disordered group is

Table 2
Selected bond lengths (Å) and angles (°) for complex **1**

Bond length			
Co–O(1)	2.085(2)	Co–O(2)	2.090(3)
Co–N(5)	2.149(2)	Co–N(3)	2.186(3)
Co–N(1)	2.191(3)	Co–N(6)	2.207(2)
Bond angle			
O(1)–Co–O(2)	176.44(9)	O(1)–Co–N(5)	90.62(11)
O(2)–Co–N(5)	92.51(11)	O(1)–Co–N(3)	92.07(10)
O(2)–Co–N(3)	89.64(10)	N(5)–Co–N(3)	89.52(12)
O(1)–Co–N(1)	85.89(10)	O(2)–Co–N(1)	92.56(10)
N(5)–Co–N(1)	87.45(12)	N(3)–Co–N(1)	176.33(9)
O(1)–Co–N(6)	89.33(10)	O(2)–Co–N(6)	87.52(10)
N(5)–Co–N(6)	179.24(16)	N(3)–Co–N(6)	91.23(13)
N(1)–Co–N(6)	91.79(13)		

Table 3
Selected bond lengths (Å) and angles (°) for complex **2**

Bond length			
Ni–O(1)	2.063(2)	Ni–O(2)	2.082(2)
Ni–N(5)	2.1046(18)	Ni–N(3)	2.118(3)
Ni–N(6)	2.1574(18)	Ni–N(1)	2.155(3)
Bond angle			
O(1)–Ni–O(2)	176.61(10)	O(1)–Ni–N(5)	90.14(10)
O(2)–Ni–N(5)	92.19(11)	O(1)–Ni–N(3)	92.94(10)
O(2)–Ni–N(3)	89.54(10)	N(5)–Ni–N(3)	89.41(12)
O(1)–Ni–N(6)	90.14(10)	O(2)–Ni–N(6)	87.50(10)
N(5)–Ni–N(6)	179.17(15)	N(3)–Ni–N(6)	91.36(12)
O(1)–Ni–N(1)	85.96(9)	O(2)–Ni–N(1)	91.67(10)
N(5)–Ni–N(1)	87.79(12)	N(3)–Ni–N(1)	176.98(8)
N(6)#1–Ni–N(1)	91.45(12)		

metal atom cannot lie on either an inversion center or a twofold axis, and thus $C2/c$ is rejected. It should be noted that in the crystal structures of both **1** and **2** the Flack parameter is not zero [0.30(18) in **1** and 0.20(15) in **2**]. This is not an indication that space group Cc is incorrect, but simply shows that both sample crystals probably had a significant amount of inversion twinning. This phenomenon is quite common, and has been described in detail in the literature [16,17]. Both of the anions were found to be disordered over two slightly different positions, and so each of the four orientations was refined as an ideal rigid body. Additionally, one of the two interstitial BPEN molecules was found to be

replaced by BPY and water 40% of the time. Crystal data and additional details are provided in Table 1. Selected bond distances and angles are listed in Table 2. Hydrogen bonds and angles are listed in Table 4.

3.2. X-ray structure determination of $[(H_2O)_2Ni(BPY)(BPEN)_2] \cdot (BPEN)_{1.6} \cdot (BPY)_{0.4} \cdot 2NO_3 \cdot 4.65H_2O$

The data collection was handled in the same manner as for the Co complex. The structure was solved and refined as above. Crystal data and additional details are provided in Table 1. Selected bond distances and angles

Table 4
Hydrogen bonds for complex **1**

D–H···A	<i>d</i> (D–H)	<i>d</i> (H···A)	<i>d</i> (D···A)	∠(DHA)
O(1)–H(1A)···N(4)	0.95	1.82	2.744(4)	164.4
O(1)–H(1B)···O(12)	0.95	1.76	2.696(4)	168.3
O(2)–H(2A)···N(2)	0.95	1.89	2.786(4)	155.2
O(2)–H(2B)···O(10')	0.95	1.74	2.682(15)	169.5
O(2)–H(2B)···O(10)	0.95	1.77	2.690(5)	162.5
O(9)–H(9A)···O(5')	0.95	1.71	2.607(19)	155.7
O(9)–H(9A)···O(5)	0.95	2.06	2.921(6)	150.0
O(9)–H(9B)···O(8')	0.95	1.70	2.585(12)	152.6
O(9)–H(9B)···O(8)	0.95	2.19	3.013(7)	143.7
O(10)–H(10A)···O(11)	0.95	1.88	2.705(6)	143.9
O(10)–H(10B)···O(7)	0.95	2.04	2.860(10)	144.2
O(11)–H(11A)···O(12)	0.95	1.99	2.810(4)	143.9
O(11)–H(11B)···N(7)	0.95	1.84	2.788(5)	172.0
O(12)–H(12A)···N(8)	0.95	1.80	2.728(5)	165.3
O(12)–H(12B)···O(4')	0.95	1.82	2.663(17)	146.1
O(12)–H(12B)···O(4)	0.95	1.85	2.745(5)	156.1

Table 5
Hydrogen bonds for complex **2**

D–H···A	<i>d</i> (D–H)	<i>d</i> (H···A)	<i>d</i> (D···A)	∠(DHA)
O(1)–H(1A)···N(4)#3	0.95	1.81	2.747(4)	167.5
O(1)–H(1B)···O(12)#4	0.95	1.76	2.702(4)	172.3
O(2)–H(2A)···N(2)#5	0.95	1.90	2.812(3)	159.5
O(2)–H(2B)···O(10')	0.95	1.76	2.691(15)	166.9
O(2)–H(2B)···O(10)	0.95	1.76	2.685(5)	165.2
O(9)–H(9A)···O(5')	0.95	1.81	2.669(17)	148.3
O(9)–H(9A)···O(5)	0.95	2.13	2.931(6)	141.4
O(9)–H(9B)···O(8')	0.95	1.67	2.557(12)	154.5
O(9)–H(9B)···O(8)	0.95	2.13	3.016(6)	155.4
O(10)–H(10A)···O(11)	0.95	1.78	2.693(6)	161.6
O(10)–H(10B)···O(7)#6	0.95	1.92	2.838(9)	160.7
O(11)–H(11A)···O(12)	0.95	2.09	2.798(4)	129.9
O(11)–H(11B)···N(7)	0.95	1.86	2.789(4)	165.8
O(12)–H(12A)···N(8)#6	0.95	1.79	2.709(4)	160.6
O(12)–H(12B)···O(4')	0.95	1.71	2.632(16)	163.7
O(12)–H(12B)···O(4)	0.95	1.82	2.746(5)	164.5

are listed in Table 3. Hydrogen bond distances and angles are listed in Table 5.

4. Results and discussion

The complexes **1** and **2** were synthesized by using the same starting ratio and reaction conditions as that of the zinc complex [7]. The crystal structures of **1** and **2** are isomorphous and isostructural. As we projected, they are the analogs of the zinc complex [7]. The structure of **1** consists of octahedral cobalt atoms coordinated by two BPY linear molecules creating a linear BPY–Co–BPY chain which extends along the *b*-axis. The BPY–Co–BPY chains are then linked by double BPEN linear chains through bifunctional covalent and hydrogen bonding interactions to form a 2-D framework structure. The basic part of **1** showing the numbering scheme is shown in Fig. 2 and the 2-D network structure of **1** is shown in Fig. 3. Two water molecules coordinate the remaining two sites around the cobalt metal atoms. The water molecules form hydrogen bonds to the non-coordinated nitrogen atoms on the double BPEN bridging molecules (O(1)–H(1A)···N(4) 2.744(4); O(2)–H(2A)···N(2) 2.786(4) Å). Each of the double bridging BPEN molecules thus contains both coordinated and hydrogen-bonded N-donors (Fig. 4): The two BPEN molecules are paired at each terminal side with one nitrogen atom covalent-bonded to the metal and one nitrogen atom hydrogen-bonded to the oxygen on the water molecule. This bifunctional double head and tail connection feature propagates to link the chains into a 2-D network (Fig. 3). Although single hydrogen-bonded organic spacers have been observed in several compounds such as [Cu(μ-4,4'-bipy)(H₂O)₂(F₃B)₂·4,4'-bipy [18], [Mn(CO)₃(μ₃-OH)]₄·2(4,4'-bipy)·2MeCN [19], and Co(NCS)₂(4,4'-bipy)(H₂O)₂·4,4'-bipy [20], the

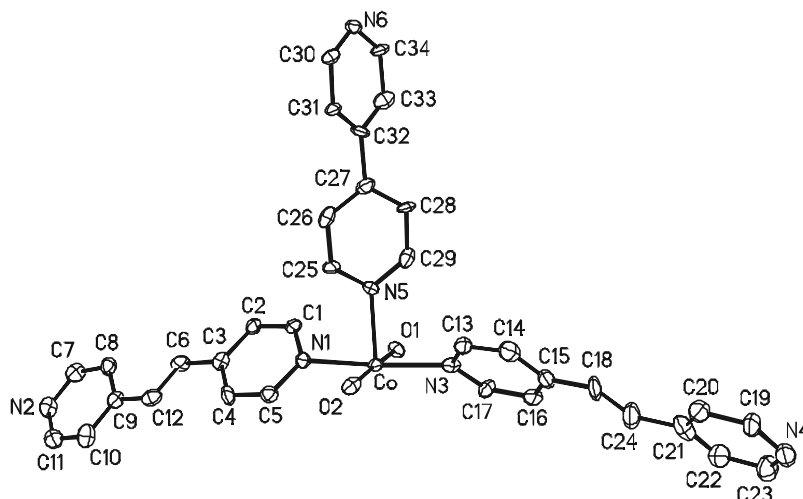


Fig. 2. View of the basic part of the polymer showing the atom numbering scheme. Thermal ellipsoids are 40% equiprobability envelopes, with hydrogen atoms omitted. This unit has essentially twofold symmetry.

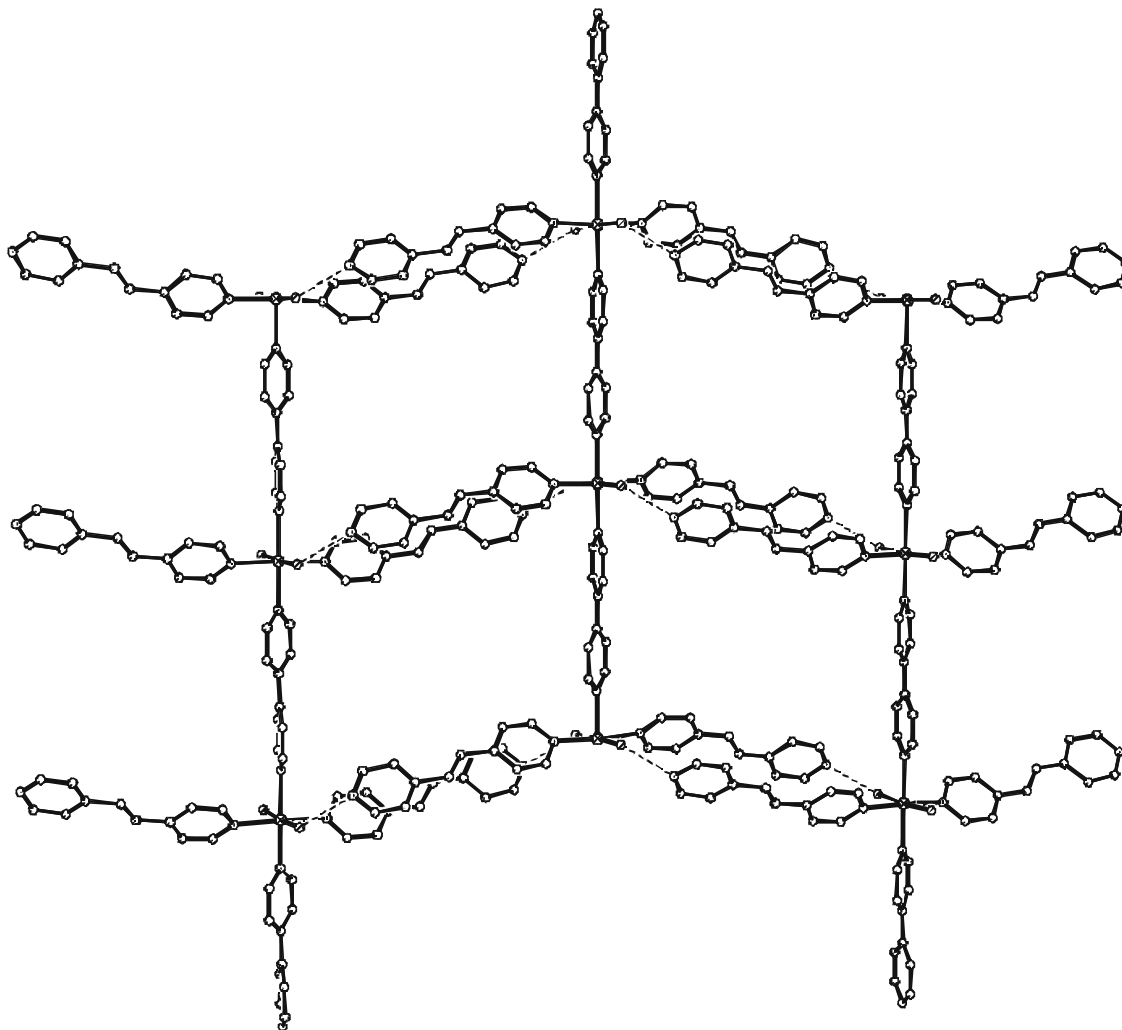


Fig. 3. View of polymer chains and the networks showing the large rectangular grids where anions and various solvent molecules reside.

double bridging feature with both covalent and hydrogen bonds observed in this system is interesting. The BPY–Co–double BPEN–Co linkages in this mixed ligand network creates large rectangles with sides of length of approximate $11.40 \times 13.10 \text{ \AA}$ (Fig. 3), which are occupied by the anions and various solvent molecules. The 2-D networks are assembled in such a way that the cobalt atoms are located close to the centers of the rectangular grid of the adjacent 2-D nets. There are about 34.6 molecules and anions (molecules included are 6.4 BPEN, 1.6 BPY, eight nitrates and 18.6 water molecules) in the cavities per unit cell volume. One of the interstitial BPEN solvent molecules was found to be replaced by BPY and water 40% of the time (see Fig. 5).

Numerous hydrogen-bonding interactions among the inclusion species are present in the structure. A total of 64 hydrogen-bonding interactions are present per unit cell volume.

The included BPY, BPEN, nitrates, and water molecules in the network structure are unsymmetrically arranged on the two sides of the BPY–Co–BPY chains (see Fig. 1), which disrupt the twofold symmetry of the network and result in a noncentrosymmetric coordination polymer. This feature can be very well sustained in this synthetic approach, which was originally found in the analogous zinc and cadmium complexes [7]. This mixed-ligand, mixed-bonding, noncentrosymmetric inclusion framework polymer created by unbalanced

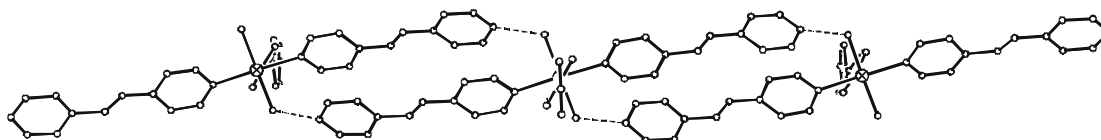


Fig. 4. View of the bifunctional BPEN molecules in the structure.

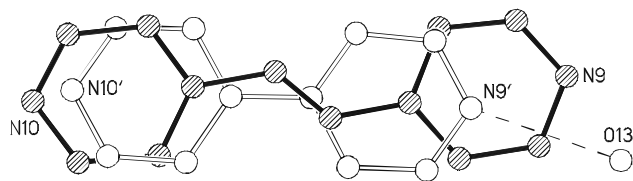


Fig. 5. View showing the arrangement of molecules in the disordered N9/N10 area, having 60% BPEN and 40% BPY + water.

inclusion guest species displays three different bonding modes of the organic molecules: pure covalent bonding mode along the BPY–Co–BPY chains; bifunctional BPEN molecules coordinated to the metal centers; and pure hydrogen bonding from the inclusion guest BPY and BPEN molecules.

Thermal analyses reveal that both complexes **1** and **2** lose guest molecules below 180 °C and gradually lose coordinating building blocks between 180 and 300 °C.

In summary, we have synthesized two new noncentrosymmetric inclusion rectangular grid framework coordination polymers. Although the covalent coordination framework has a virtual twofold axis, the included hydrogen bonding species revealed noncentrosymmetric property. The creation of the acentricity by guest species may well be worth of further explorations in metal–organic polymer research. Our research in this direction and the utilization of multi-functional bonding-mode of organic ligands are in progress.

5. Supplementary data

Crystallographic data have been deposited with The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +33-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>) and are available on request quoting the deposition number CCDC-164290 and CCDC-164291 for compounds **1** and **2**.

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