

A New Route for Preparing Coordination Polymers from Hydrothermal Reactions Involving in Situ Ligand Synthesis

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The coordination chemistry of inorganic cobalt salt and the organic ligands H₄bbh (=benzene-1,2,4,5-bihydrazide) and H₃bcbh (=benzene-4-carboxylate-1,2-bihydrazide) generated through the in situ hydrothermal acylate reaction of H₄bta (=benzene-1,2,4,5-tetracarboxylic acid) and H₃btc (=benzene-1,2,4-tricarboxylic acid) with hydrazine hydrate, respectively, has been investigated. Three new coordination polymers were prepared and fully characterized by infrared spectroscopy, elemental analysis, and single-crystal X-ray diffraction. The compound [Co(μ_3 -H₂bbh)(phen)]_n (**1**) (triclinic space group $P\bar{1}$ with $a = 9.762(4)$ Å, $b = 10.169(4)$ Å, $c = 11.143(4)$ Å, $\alpha = 80.96(3)^\circ$, $\beta = 64.49(3)^\circ$, $\gamma = 71.88(3)^\circ$, $Z = 2$) was synthesized from the reaction of CoCl₂·6H₂O, H₄bta (=benzene-1,2,4,5-tetracarboxylic acid), N₂H₄·H₂O, phen (=1,10-phenanthroline) and H₂O, and consists of one-dimensional double-chains. [Co(μ_4 -H₂bbh)(H₂O)₂]_n (**2**) (monoclinic space group $P2(1)/c$ with $a = 6.8687(5)$ Å, $b = 7.5943(6)$ Å, $c = 10.0401(6)$ Å, $\beta = 95.250(4)^\circ$, $Z = 2$) was generated by the combination of CoCl₂·6H₂O, H₄bta, N₂H₄·H₂O, and H₂O. It adopts a three-dimensional structural motif in the solid state with channels consisting of 20-numbered rings. [Co(μ_3 -H₃bcbh)(bpy)]_n (**3**) (monoclinic space group Cc with $a = 9.9464(13)$ Å, $b = 23.685(5)$ Å, $c = 7.9491(16)$ Å, $\beta = 117.677(13)^\circ$, $Z = 4$) was obtained from the mixture of CoCl₂·6H₂O, N₂H₄·H₂O, H₃btc (=benzene-1,2,4-tricarboxylic acid), bpy (=2,2'-dipyridyl), and H₂O, and features a two-dimensional plane. The results of magnetic research indicate that there exist antiferromagnetic interactions between Co centers in both compounds **1** and **2**.

Introduction

The connection of metal–organic coordination polymers based on complexes of transition metals and multifunctional bridging ligands has proven to be a promising field due to the intriguing network topologies and potential functions as new classes of materials.¹ Over the past decades, different classes of coordination polymers have been successfully

designed and synthesized. Recently, bridging ligands containing N- or/and O-donors, for example, multidentate aromatic polycarboxylate including benzene-1,2-dicarboxylate,² benzene-1,3-dicarboxylate,³ benzene-1,4-dicarboxylate,⁴ benzene-1,2,3-tricarboxylate,⁵ benzene-1,2,4-tricarboxylate,⁶ benzene-1,3,5-tricarboxylate,⁷ and especially ben-

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zene-1,2,4,5-tetracarboxylate,⁸ have been widely used for hydrothermal syntheses of coordination polymers of transition metals,⁹ and the syntheses are mainly through the direct interaction between the metal ion and carboxylate group to construct one-, two-, and three-dimensional networks in a variety of coordination modes. The hydro(solvo)thermal method has been proven to be a promising technique in the preparation of highly stable, infinite metal–ligand frameworks with much encouraging potential for applications, including nonlinear optics, catalysis and separation, magnetism, and molecular recognition.¹⁰ However, hydrothermal methods for modification of organic ligands are less studied. So far, five types of organic ligand reactions under hydrothermal conditions have been uncovered. They include the hydrolysis of ester or cyano groups into carboxylic groups,¹¹ substitution of a carboxylate group by a sulfonate group,¹² oxidative coupling of *o*-phenanthroline to generate a 2,2-biphenanthroline,¹³ hydroxylation of aromatic rings,¹⁴ and cycloaddition between the cyano group and the azide group anion.¹⁵ These reactions represent promising new routes for constructing novel coordination polymers under hydro(solvo)thermal conditions. We hope to synthesize new organic ligands through in situ reaction between reaction agents under hydrothermal conditions, and the organic ligands are assembled with metal ions to form coordination polymers. Derived from the known reactions, it may be expected to generate the target products by utilizing an

acylate reaction between an aromatic multicarboxyl acid and hydrazine hydrate and the stabilization of Co(II) coordination polymers containing N- and O-donor ligands. Fortunately, we obtained some novel Co(II) coordination polymers.

In this paper, we report syntheses and characterization of three new coordination polymers, $[\text{Co}(\mu_3\text{-H}_2\text{bbh})(\text{phen})]_n$ **1**, $[\text{Co}(\mu_4\text{-H}_2\text{bbh})(\text{H}_2\text{O})_2]_n$ **2**, and $[\text{Co}(\mu_3\text{-Hbcbbh})(\text{bpy})]_n$ **3**. To the best of our knowledge, these three transition metal coordination polymers containing H₃bcbh or H₄bbh bridging ligands generated via in situ acylation reaction are the first synthesized.

Experimental Section

Materials and Analyses. All reagents are of analytical grade and were used as obtained from commercial sources without further purification. IR (KBr pellets) spectra were recorded in the 225–4000 cm⁻¹ range using a Perkin-Elmer Spectrum One FTIR spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 elemental analyzer. Magnetic measurement was obtained using MPMS-XL magnetometer at *H* = 5000 Oe in the temperature range 2–300 K. XPS analysis was performed on an EASY ESCA spectrometer with an Mg K α achromatic X-ray source.

Preparation of the Complexes. $[\text{Co}(\mu_3\text{-H}_2\text{bbh})(\text{phen})]_n$ (1**).** The dark brown block crystals of **1** were synthesized hydrothermally from a mixture of CoCl₂·6H₂O, H₄bta, N₂H₄·H₂O, phen, and H₂O (molar ratio 14:21:13:8:1500) in a 30 mL Teflon-lined stainless steel autoclave (25 mL capacity) under autogenous pressure heated to 170 °C for 4 days and cooled to room temperature. Crystalline product was filtered, washed with distilled water, and dried at ambient temperature to give 0.42 g of the compound (yield 41% based on cobalt). The compound is stable and insoluble in water and most organic solvents. The XPS spectrum for the compound shows 782.7 eV of Co_{2p_{3/2}} binding energy attributed to Co²⁺. Anal. Calcd for $[\text{CoC}_{22}\text{H}_{12}\text{N}_6\text{O}_4]_n$ (**1**): C, 54.67; H, 2.50; N, 17.39%. Found: C, 54.81; H, 2.79; N, 17.01%. IR (KBr, cm⁻¹): 1647.17 s, 1557.09 w, 1496.79 s, 1431.94 m, 1362.77 s, 1290.06 s, 1179.25 s, 1143.39 m, 1058.96 m, 945.70 m, 868.80 m, 841.09 s, 809.94 s, 724.79 s, 701.48 m, 674.65 m, 656.46 m, 550.63 m, 511.67 w, 429.38 s.

$[\text{Co}(\mu_4\text{-H}_2\text{bbh})(\text{H}_2\text{O})_2]_n$ (2**).** The orange block crystal product of the compound (0.68 g, yield 46% based on cobalt) was obtained under the same reaction conditions and operations as those for **1** in a molar ratio of CoCl₂·6H₂O:H₄bta:N₂H₄·H₂O:H₂O = 2.6:5:4.5:625. The compound is stable and insoluble in water and most organic solvents. Anal. Calcd for $[\text{CoC}_{10}\text{H}_8\text{N}_4\text{O}_6]_n$ (**2**): C, 35.42; H, 2.38; N, 16.52%. Found: C, 35.11; H, 2.16; N, 16.91%. IR (KBr, cm⁻¹): 3298.82 s, 1605.70 s, 1504.72 s, 1384.57 s, 1326.70 w, 1305.67 s, 1181.43 s, 1149.88 s, 1060.12 s, 932.23 m, 902.57 s, 828.06 s, 761.35 s, 694.96 w, 679.55 m, 622.99 m, 562.08 s, 434.98 s, 421.50 w.

$[\text{Co}(\mu_3\text{-Hbcbbh})(\text{bpy})]_n$ (3**).** The dark brown block crystals of **3** were synthesized hydrothermally from a mixture of CoCl₂·6H₂O, N₂H₄·H₂O, H₃btc, bpy (=2,2-bipyridine) and H₂O in a molar ratio 14:21:13:1500 in a 30 mL Teflon-lined stainless steel autoclave (25 mL capacity) under autogenous pressure heated to 170 °C for 4 days and cooled naturally to room temperature. The obtained dark brown crystals were isolated by filtration and washed with distilled water (0.52 g, yield 41% based on cobalt). The compound, as compounds **1** and **2**, is also stable and insoluble in water and most organic solvents. Anal. Calcd for $[\text{CoC}_{19}\text{H}_{12}\text{N}_4\text{O}_4]_n$ (**3**): C, 54.43; H, 2.88; N, 13.36%. Found: C, 54.21; H, 2.58; N, 13.63%. IR

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Table 1. Crystal Data and Structure Refinement Details for Compounds **1**, **2**, and **3**

	1	2	3
empirical formula	[CoC ₂₂ H ₁₂ N ₆ O ₄] _n	[CoC ₁₀ H ₈ N ₄ O ₆] _n	[CoC ₁₉ H ₁₂ N ₄ O ₄] _n
<i>T</i> , K	293(2)	293(2)	293(2)
λ (Mo K α), Å	0.71073	0.71073	0.71073
cryst size, mm ³	0.40 × 0.26 × 0.26	0.21 × 0.16 × 0.12	0.50 × 0.32 × 0.32
cryst syst	triclinic	monoclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> 2(1)/ <i>c</i>	<i>C</i> <i>c</i>
<i>a</i> , Å	9.762(4)	6.8687(5)	9.9464(13)
<i>b</i> , Å	10.169(4)	7.5943(6)	23.685(5)
<i>c</i> , Å	11.143(7)	10.0401(6)	7.9491(16)
α , deg	80.96(3)	90	90
β , deg	64.49(3)	95.250(4)	117.677(13)
γ , deg	71.88(3)	90	90
<i>V</i> , Å ³	948.4(7)	521.52(6)	1658.4(5)
<i>Z</i>	2	2	4
<i>D</i> _{calc} , Mg m ⁻³	1.692	2.160	1.679
μ , mm ⁻¹	0.953	1.689	1.072
R1/wR2			
obsd data ^a	0.0402/0.1040	0.0277/0.0799	0.0289/0.0779
all data ^a	0.0491/0.1072	0.0316/0.0819	0.0303/0.0800
data collections, deg	4.06 ≤ 2θ ≤ 51.96	5.96 ≤ 2θ ≤ 46.44	3.44 ≤ 2θ ≤ 51.98
reflins collected	4533	2395	2059
indep reflins	3703	751	1921
reflins with <i>I</i> > 2 σ (<i>I</i>)	3096	667	1827
data/restraints/params	3703/0/346	751/0/105	1921/2/301

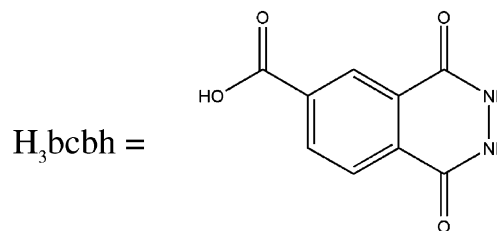
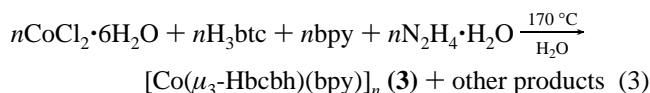
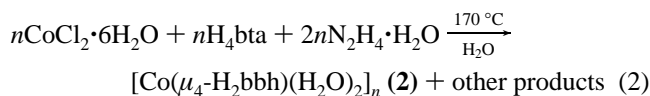
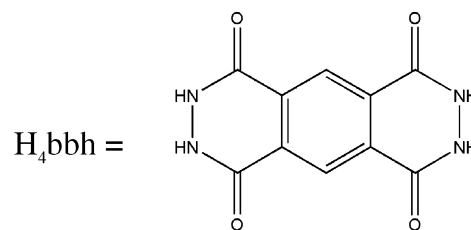
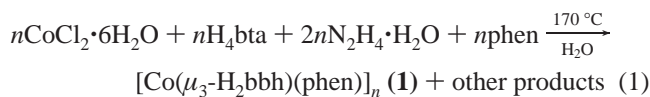
$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$$

(KBr, cm⁻¹): 1579.11 w, 1550.61 s, 1477.31 w, 1443.52 w, 1380.87 s, 1334.45 w, 1303.52 s, 1248.23 w, 1222.12 m, 1152.12 m, 1128.30 m, 1086.18 w, 1059.32 w, 1022.09 m, 937.10 w, 868.22 w, 845.61 m, 790.08 s, 771.40 s, 737.45 m, 708.50 m, 651.82 w, 630.71 w, 530.14 w, 422.43 s.

Crystallographic Analyses. Suitable single crystals of **1–3** were selected and mounted in air onto thin glass fibers. X-ray intensity data for **1** and **3** were measured at 293 K on a Siemens P4 diffractometer (Mo K α , $\lambda = 0.71073$ Å). Data collections for **2** were performed at 293 K on a Bruker-AXS Smart CCD diffractometer (Mo K α , $\lambda = 0.71073$ Å). The raw frame data for **1–3** were integrated into SHELEX-format reflection files and corrected for Lorentz and polarization effects using SAINT. Corrections for incident and diffracted beam absorption effects were applied using SADABS. None of the crystals showed evidence of crystal decay during data collection. Compound **1–3** crystallized in the space group *P* $\bar{1}$, *P*2(1)/*c*, and *C**c*, respectively, as determined by the systematic absences in the intensity data, intensity statistics, and the successful solution and refinement of the structures. All structures were solved by a combination of direct methods and difference Fourier syntheses and refined against *F*² by the full-matrix least-squares technique. Details of the crystal data, intensity collection, and refinement for compounds **1**, **2**, and **3** are listed in Table 1. Selected interatomic distances (Å) and angles (deg) for the coordination environment of the cobalt atom in compounds **1**, **2**, and **3** are listed in Table 2.

Results and Discussion

Syntheses. The acylation reactions of H₄bta and H₃btc took place, respectively, during formation of compound **1**, **2**, and **3**. Formation reactions are given as follows, respectively:



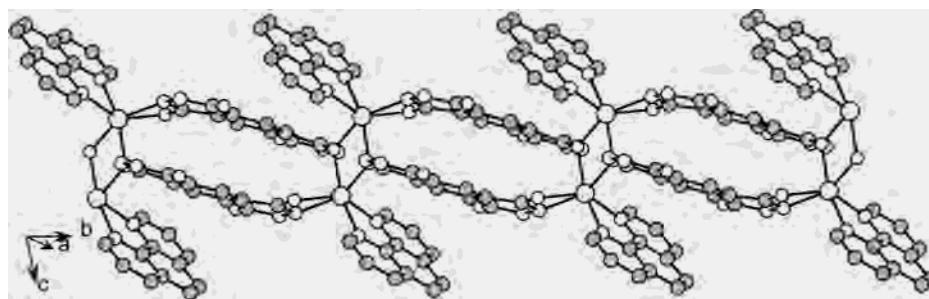
The formations of the crystal product of compounds **1–3** were under hydrothermal conditions with in situ reaction. The preparation depends on the choices of proper synthesis conditions, in which pH value is vital, and the required reaction temperature is commonly 170 °C to 200 °C. No crystal products of compounds **1–3** were obtained when the pH value of the reaction system seriously deviated from 6.0. We attempted to prepare iron and nickel analogues of compounds **1–3** through replacing CoCl₂·6H₂O with FeCl₂·4H₂O and NiCl₂·6H₂O under similar reaction conditions, respectively, but were not successful. We also tried to synthesize other aromatic multicarboxyl acids analogues of compounds **1–3** using benzene-1,2-dicarboxylate, benzene-1,3-dicarboxylate, benzene-1,4-dicarboxylate, etc. but failed. The reason for the latter may be the instability of seven- and eight-membered rings. We failed to get the analogue of compounds **1–3** through substituting phenyl hydrazine for hydrazine hydrate, also. The reason may be the constraints of the steric effect of phenyl hydrazine. We tried for many times to use preformed hydrazide ligands of relevant multicarboxylic acids to prepare the target compounds, but these efforts failed, too.

Structural Description. [Co(μ₃-H₂bbh)(phen)]_n (**1**). Single-crystal X-ray analysis has revealed that compound **1** possesses a one-dimensional double-chain structure, as shown in Figure 1. The coordination sphere of the Co (II) site is defined by three acyl oxygen atoms O(2), O(3), and O(3A), one acylamino nitrogen atom N(5), and two nitrogen atoms N(1) and N(2) from phen, leading to a distorted octahedron geometry, as displayed in Figure 2. In the coordination environment, N(5) and O(2), and N(1) and N(2) simulta-

Table 2. The Coordination Environment of the Cobalt Atom in Compounds **1**, **2**, and **3**. Selected Interatomic Distances (Å) and Angles (deg)

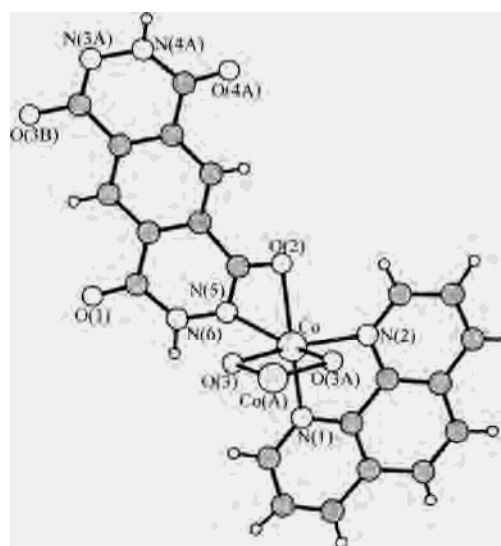
1					
Co–O(3)	2.070(2)	Co–N(1)	2.149(2)	N(3)#2–N(4)#2 ^a	1.387(3)
Co–O(3)#1	2.099(2)	Co–N(2)	2.150(3)	N(5)–N(6),	1.401(3)
Co–O(2)	2.125(2)	Co–N(5)	2.260(2)	Co···Co#1	3.296(4)
O(3)–Co–O(3)#1	75.49(8)	O(3)–Co–N(2)	87.95(9)	O(3)#1–Co–N(5)	86.32(8)
O(3)–Co–O(2)	106.24(8)	O(3)#1–Co–N(2)	163.39(8)	O(2)–Co(1)–N(5)	60.14(8)
O(3)–Co–O(2)	98.50(8)	O(2)–Co–N(2)	87.18(9)	N(1)–Co–N(5)	95.90(9)
O(3)#1–Co–N(1)	105.74(9)	N(1)–Co–N(2)	76.85(10)	N(2)–Co–N(5)	109.92(9)
O(2)–Co–N(1)	144.75(9)	O(3)–Co–N(5)	155.69(8)	O(3)–Co–N(1)	104.38(8)
2					
Co–O(2)#1	2.089(2)	Co–N(1)	2.128(3)	Co(1)–Ow1#1	2.145(2)
Co–O(2)	2.089(2)	Co–N(1)#1	2.128(3)	Co(1)–Ow1	2.145(2)
O(2)#1–Co–O(2)	180.00(12)	N(1)–Co–N(1)#1	180.0(2)	O(2)#1–Co–Ow1	82.84(9)
O(2)#1–Co–N(1)	89.44(9)	O(2)#1–Co–Ow1#1	97.16(9)	O(2)–Co–Ow1	97.16(9)
O(2)–Co–N(1)	90.56(9)	O(2)–Co–Ow1#1	82.84(9)	N(1)–Co–Ow1	87.65(10)
O(2)#1–Co–N(1)#1	90.56(9)	N(1)–Co–Ow1#1	92.35(10)	N(1)#1–Co–Ow1	92.35(10)
O(2)–Co–N(1)#1	89.44(9)	N(1)#1–Co–Ow1#1	87.65(10)	Ow1#1–Co–Ow1	180.0
3					
Co–O(1)	2.769(5)	Co–N(4)	2.057(3)	Co–N(1)	2.094(3)
Co–O(2)	2.056(3)	Co–O(3)	2.092(3)	Co–N(2)	2.144(3)
O(2)–Co–N(4)	128.02(15)	O(2)–Co–N(1)	98.89(14)	N(4)–Co–N(2)	87.15(12)
O(1)–Co–O(3)	90	N(4)–Co–N(1)	130.70(12)	O(3)–Co–N(2)	167.01(11)
O(2)–Co–O(3)	99.79(12)	O(3)–Co–N(1)	94.38(11)	N(1)–Co–N(2)	76.63(12)
N(4)–Co–O(3)	91.89(11)	O(2)–Co–N(2)	90.95(13)	O(1)–C(18)–O(2)	123.8(4)

^a Symmetry transformations used to generate equivalent atoms: **(1)** #1 $-x, -y + 1, -z + 2$; #2 $x, y - 1, z$; #3 $x, y + 1, z$. **(2)** #1 $-x + 1, -y, -z$; #2 $-x + 1, y + 1/2, -z + 1/2$; #3 $-x + 2, -y, -z + 1$; #4 $-x + 1, y - 1/2, -z + 1/2$. **(3)** #1 $x + 1, y, z$; #2 $x, -y + 1, z - 1/2$; #3 $x - 1, y, z$; #4 $x, -y + 1, z + 1/2$.

**Figure 1.** View of the double chain structure of compound **1**.

neously chelate the cobalt atom, while O(3) and O(3A) adopt a bidentate bridging mode connecting two cobalt atoms. N(6), O(1), O(4A), N(3A), and N(4A) are not coordinated to the Co(II) atom. The whole H₂bbh ligand shows a μ_3 -coordination mode. No hydrogen atoms were found at N(3A) and N(5), and the hydrogen atoms attached to C, N(4A), and N(6) were accurately located. The neighboring cobalt atoms are held together by the bridging acyl oxygen atoms with Co–Co(A) distances of 3.296(4) Å. It is very interesting that Co₂O₂ cores including Co, Co(A), O(3), and O(3A) in parallelogram geometry are interconnected via H₂bbh bridging ligands to generate a centipede-like double-chain structure, propagated along the *b* axis direction. In the double-chain, the planes of two H₂bbh ligands between each two Co₂O₂ cores are parallel to each other and perpendicular to the *bc* plane. The phen rings as auxiliary ligands on the same side of the chain are also parallel to each other.

[Co(μ_4 -H₂bbh)(H₂O)₂]_{*n*} (**2**). As shown in Figure 3, The Co(II) atom in **2** is coordinated by two acyl oxygen atoms from two H₂bbh ligands with a Co–O distance of 2.089(2)

**Figure 2.** The coordination environment of the cobalt atom in compound **1**.

Å, two acylamino nitrogen atoms from two H₂bbh ligands with a Co–N distance of 2.128(3) Å, and two water

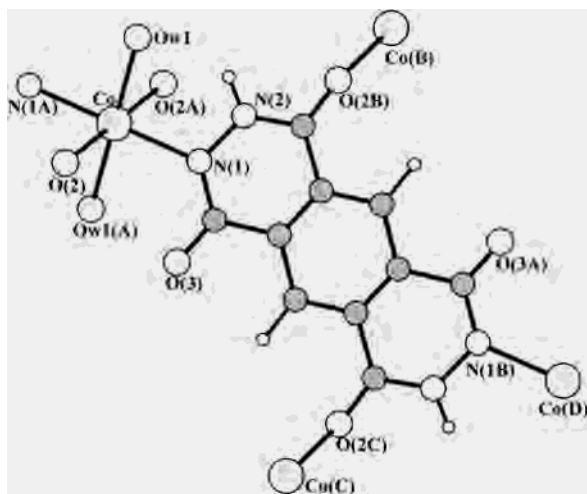


Figure 3. The coordination environment of the cobalt atom in compound 2.

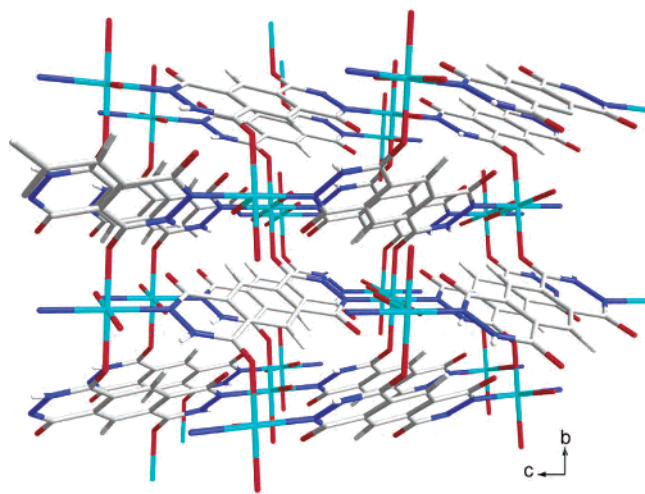


Figure 4. The packing diagram along the [100] direction for compound 2.

molecules with a Co—Ow1 distance of 2.145(2) Å, forming a slightly distorted octahedron geometry. The whole H₂bbh ligand displays a μ_4 -coordination mode through acyl oxygen and acylamino nitrogen linking with four Co(II) atoms.

Figure 4 shows the 3-D structure of compound 2, and from the figure it can be seen that Co atoms and H₂bbh ligands are alternately interconnected into a 2-D layer, and then 2-D layers are interlinked again to form the 3-D structure. Both Co and H₂bbh ligands can be divided into two classes. Each of the first kind of Co atoms is connected with four H₂bbh ligands in the same 2-D layer, and each of second one is connected with two H₂bbh in the same 2-D layer and two H₂bbh in neighboring layers. Similarly, each of the first class of H₂bbh ligands is linked to four Co atoms in an identical layer, and each of the second one is linked two Co atoms in an identical layer and two Co atoms in neighboring layers. Through the second kind of Co atoms and H₂bbh ligands, 2-D layers are interconnected into the 3-D framework, in which there exist channels that cross each other.

[Co(μ_3 -Hbcbh)(bpy)]_n (3). The structure of compound 3 consists of a two-dimensional neutral framework structure (Figure 5). Along the crystallographic *c* axis, acyl hydrazine

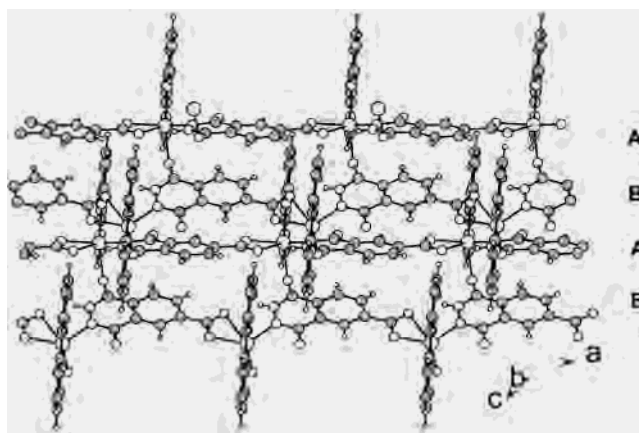


Figure 5. The neutral framework view of compound 3 [010] projection.

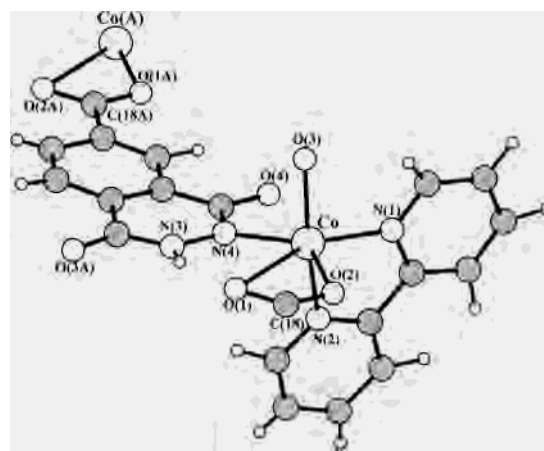


Figure 6. The coordination environment of the cobalt atom in 3.

nitrogen atoms without hydrogen are bridged to Co(II) atoms. Carboxylate oxygen atoms adopt a bidentate chelating mode, chelating cobalt atoms along the *a* axis. The acyl hydrazine oxygen atoms are coordinated to Co(II) atoms. The whole Hbcbh ligand displays the μ_3 -coordination mode. It is noticeable that the two kinds of Hbcbh ligand layers [A layer and B layer, both possess the same coordinate mode] are arranged alternately. The angle between the A layer and the B layer is about 56°. The A layers and the B layers, respectively, are parallel to each other and the bpy rings as auxiliary ligands are parallel to each other, too. The Co(II) atom environment in the compound can be described as a distorted octahedron geometry (Figure 6) with two carboxylate oxygen atoms [O(1) and O(2)] from Hbcbh, one Hbcbh-nitrogen atom [N(4)] and one bpy-nitrogen atom [N(1)] that comprise the equatorial plane, whereas the axial positions are filled by an acyl oxygen [O(3)] of Hbcbh and a bpy-nitrogen [N(2)].

Magnetic Properties. Compound 1. The magnetic behavior of compound 1 under the form of χ_M and μ_{eff} versus *T* plots is shown in Figure 7. Upon cooling the temperature, the molar magnetic susceptibility χ_M increases smoothly to a maximum of 0.0722 cm³ mol⁻¹ at 10 K, and then decreases slightly. Furthermore the χ_M value increases below 6 K, probably due to a paramagnetic impurity, which are often

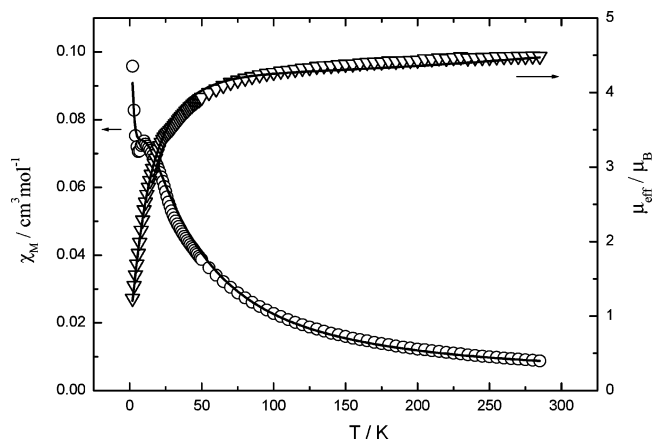


Figure 7. Experimental (○ and ▽) and fitted (—) temperature dependence of χ_M and μ_{eff} for compound **1**.

observed (ref 16) in cobalt(II) compounds. The effective magnetic moment (μ_{eff}) at 300 K is $4.49 \mu_B$. This value is larger than the spin-only value of high-spin cobalt(II) ($3.87 \mu_B$, $\mu_{\text{iso}} = [4S(S + 1)]^{1/2}$, $S = 3/2$), but less than the value expected when the spin momentum and the orbital momentum exist independently [$5.20 \mu_B$, $\mu_{\text{LS}} = [L(L + 1) + 4S(S + 1)]^{1/2}$, $L = 3$, $S = 3/2$]. The μ_{eff} value continuously decreases from room temperature to $1.24 \mu_B$ at 2.0 K. Therefore, the decrease of magnetic moments with lowering temperature was mainly due to three possible factors: (i) an intramolecular antiferromagnetic coupling between two Co(II) centers, (ii) an intermolecular antiferromagnetic coupling along the chains, and (iii) the contribution of the orbital momentum. Experiment magnetic data has been fitted.

Compound 2. The dependence of the magnetic susceptibility of compound **2** on the temperature in the range of 2–300 K was studied. As illustrated in Figure 8, the μ_{eff} value at 300 K is $4.53 \mu_B$, which is larger than that of compound **1**. This indicates a contribution of the orbital momentum typical for the $^4T_{1g}$ ground state. Upon cooling, the μ_{eff} slowly decreases from $4.53 \mu_B$ at room temperature to $2.27 \mu_B$ at 2.0 K. The values are typical for cobalt(II) ion in an octahedral environment with an enhanced moment due to orbital contribution and a lowering of the moment at low temperature due to the effect of spin–orbital coupling.¹⁷ The χ_M value starts at $0.00851 \text{ cm}^3 \text{ mol}^{-1}$ at room temperature and increases in a uniform way to $0.322 \text{ cm}^3 \text{ mol}^{-1}$ at 2 K.

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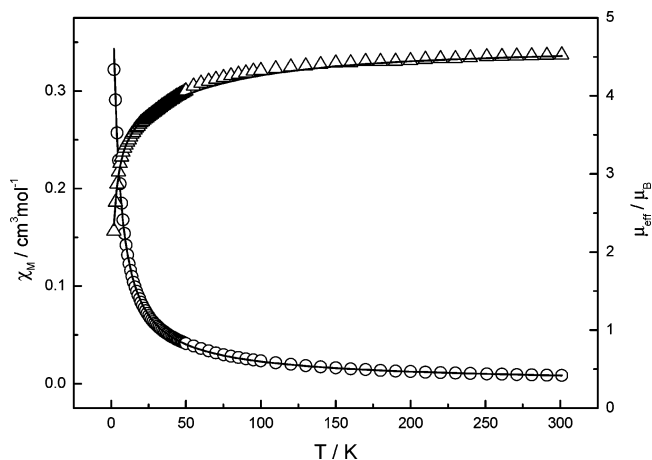


Figure 8. Experimental (○ and Δ) and fitted (—) temperature dependence of χ_M and μ_{eff} for compound **2**.

The absence of a maximum in this χ_M curve may indicate that the possible antiferromagnetic coupling is very weak.¹⁸ Experimental magnetic data has been fitted.

Conclusions. The reactivity of organic ligands under hydrothermal conditions shows some differences from those under usual conditions; thus modification of organic ligands under hydrothermal conditions is very promising in the synthesis of useful new ligands. The work here provides strong encouragement that a wide variety of coordination polymers can be produced by in situ hydrothermal generation of bridging ligands in the presence of appropriate metal ions, although it is a great challenge to develop to the stage where a desired structure or crystal symmetry can be ensured.

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Supporting Information Available: X-ray crystallographic files in CIF format, figures of some relevant structures, magnetic data fitting, and discussion. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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