One- and Three-Dimensional Coordination Polymers Containing Organic Ligands Produced Through in situ Hydrothermal Reactions

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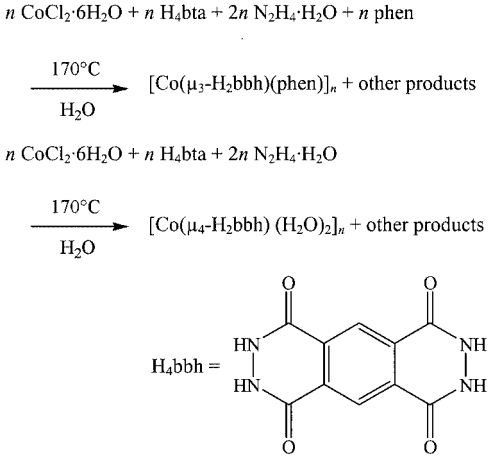
Two novel coordination polymers of cobalt(II), $[Co(\mu_3\text{-}H_2bbh)(phen)]_n$ (**1**) and $[Co(\mu_4\text{-}H_2bbh)(H_2O)_2]_n$ (**2**) (phen = 1,10-phenanthroline; H_4bbh = benzene-1,2,4,5-tetracarbo-1,2:4,5-dihydrazide), in which H_2bbh ligands are in situ generated by an acylation reaction of H_4bta (H_4bta = benzene-1,2,4,5-tetracarboxylic acid) with hydrazine hydrate under hydrothermal conditions have been synthesized and structurally characterized.

Introduction

The construction of metal-organic coordination polymers based on complexes of transition metals and multifunctional bridging ligands has proven to be an interesting field due to the intriguing network topologies and potential functions of this new class of materials.[1] Bridging ligands containing N-, and/or O-donors, for example multidentate aromatic polycarboxyl systems, including benzene-1,3-dicarboxylate,[2] -1,4-dicarboxylate,[1a,3] -1,2,3-tricarboxylate,[4] -1,2,4-tricarboxylate,[5] -1,3,5-tricarboxylate,[6] and especially benzene-1,2,4,5-tetracarboxylate,[7] have been widely used for hydrothermal syntheses of coordination polymers of metals,[8] and the syntheses occur mainly through direct interaction between the metal ion and the carboxylate group to construct one-, two- and three-dimensional networks in a variety of coordination modes. The hydro(solvo)thermal method has proved to be a promising technique in the preparation of highly stable, infinite metal−ligand frameworks[9] and the modification of organic ligands. So far, five types of organic ligand reactions under hydrothermal conditions have been uncovered, namely hydrolysis of ester or cyano groups into carboxylate groups,[8a,8c,9] substitution of a carboxylate group by a sulfonate group,[10] oxidative coupling of *o*-phenanthroline to generate a 2,2-biphenanthroline,[11] hydroxylation of aromatic rings[8b,12] and cycloaddition between the cyano group and the azide groups.[13] These reactions represent promising new routes for constructing novel coordination polymers under hydro(solvo)thermal condition.

We wanted to synthesize novel coordination polymers containing new ligands produced through an in situ reaction between the reactants under hydrothermal condition. Based on known reactions, it may be expected that generation of the target products could be achieved by utilizing an acylation reaction between benzene-1,2,4,5-tetracarboxylate and hydrazine hydrate.

Fortunately, we obtained two novel Co^{II} coordination polymers, $[Co(\mu_3\text{-}H_2bbh)(phen)]_n$ (**1**) and $[Co(\mu_4\text{-}H_2bbh)(H_2O)_2]_n$ (**2**). To the best of our knowledge, these are the first two examples in which new organic ligands have been generated by acylation and coordinated by transition metal ions to form novel polymers. Scheme 1 depicts equations representing the formation of the two compounds.



Scheme 1

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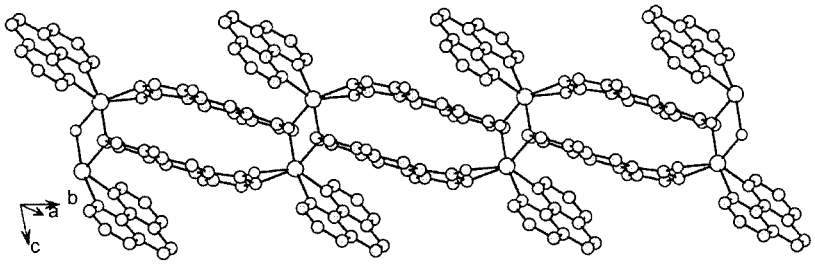

Figure 1. View of the double-chain structure of compound **1**

Results and Discussion

A single-crystal X-ray diffraction study revealed that compound **1** possesses a one-dimensional double-chain structure, as shown in Figure 1.

As shown in Figure 2, 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 octahedral geometry. In the coordination environment, N(5) and O(2), and N(1) and N(2) chelate the cobalt atom, while O(3) and O(3A) adopt a bidentate bridging mode connecting two cobalt atoms. The H_2bbh ligand shows a μ_3-coordination mode. No hydrogen atoms were found at N(3A) and N(5) by single-crystal X-ray analysis but 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 the Co_2O_2 cores including Co, Co(A), O(3) and O(3A) in adopting a parallelogram geometry are interconnected by H_2bbh bridging ligands to generate a centipede-like double-chain structure propagated along the *b* axis direction. In the double-chain, the planes of two H_2bbh ligands between each two Co_2O_2 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.

As shown in Figure 3, the Co^{II} atom environment in **2** can be described as octahedral (Figure 3) with two acyl oxygen atoms [O(2) and O(2A)] from $[H_2bbh]^{2-}$ and two H_2O groups that comprise the equatorial plane, with the axial positions being occupied by two nitrogen atoms [N(1) and N(1A)] from $[H_2bbh]^{2-}$. The H_2bbh ligand displays a μ_4-coordination mode through an acyl oxygen atom and an acylamino nitrogen atom linking with four Co^{II} atoms.

Figure 4 shows the 3-D structure of compound **2** and Figure 5 shows a schematic representation revealing the 4-connected topology of the 3-D network of **2**. From these figures it can be seen that the Co atoms and H_2bbh ligands are alternately interconnected into 2-D sheets and these sheets are again interlinked to form the 3-D structure. Specifically, both the Co centers and the H_2bbh ligands can be divided into two classes. Each of the first type of Co atoms is connected to four H_2bbh ligands in the same layer, and each of the second type is connected to two H_2bbh ligands in the same layer and two H_2bbh groups in neighboring layers. Similarly, each of the first class of H_2bbh ligands is linked to four Co centers in the same layer, and each of the second type is linked to two Co centers in the

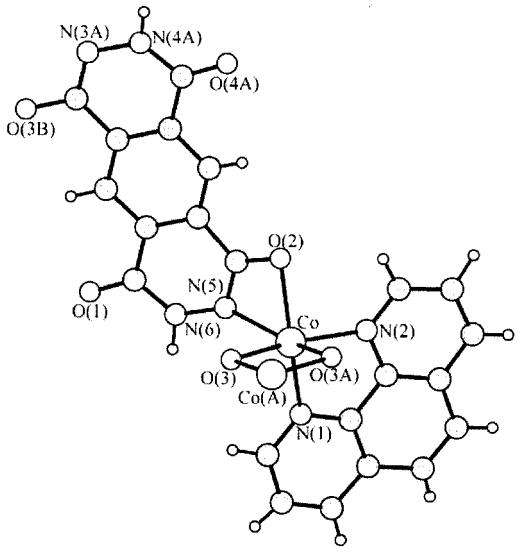

Figure 2. Coordination environment of the cobalt atom in compound **1**; selected interatomic distances [Å]: Co−O(3) 2.070(2), Co−O(3A) 2.099 (2), Co−O(2) 2.125(2), Co−N(1) 2.149(2), Co−N(2) 2.150(3), Co−N(5) 2.260(2), Co···Co 3.296(4); symmetry code A: $-x$, $-y + 1$, $-z + 2$

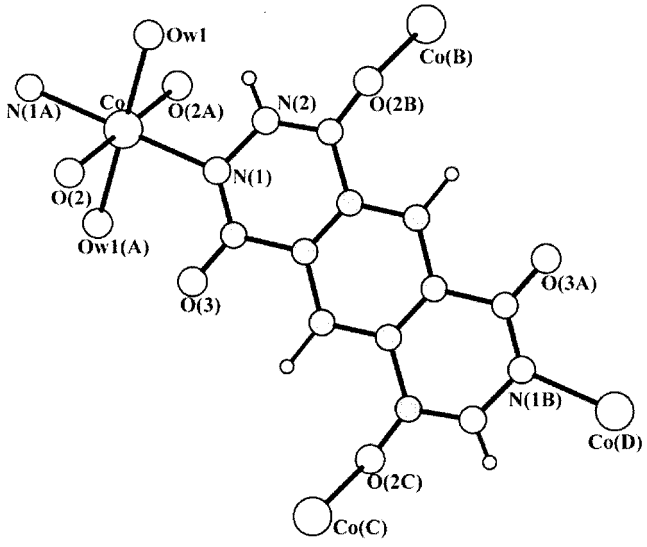

Figure 3. Coordination environment of the cobalt atom in compound **2**; selected interatomic distances [Å]: Co−O(2) 2.089(2), Co−N(1) 2.128(3), Co−O(w1) 2.145(2); symmetry code A: $-x$, $-y$, $-z$

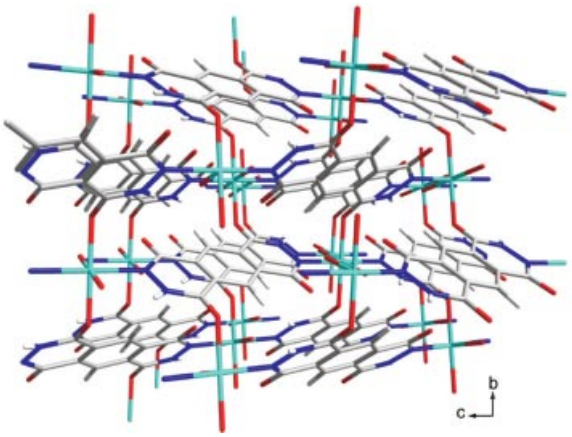

Figure 4. Packing diagram along the [100] direction for compound **2**

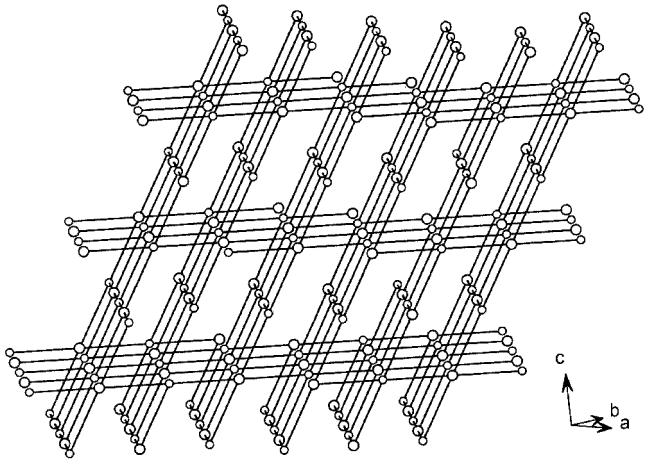

Figure 5. Representation showing the topology of the 3-D network for **2**; the H_2bbh ligands are shown as filled large circles and the cobalt atoms as open small cycles

same layer and two Co centers in neighboring layers. Through the second type of Co atoms and H_2bbh ligands, the layers are intergrated into the 3-D framework. Figure 4 indicates that in the solid state of **2**, there exist channels constructed of 22-membered rings consisting of three Co atoms and three H_2bbh ligands. In fact, the channels are intertwined in the 3-D network (Figure 5).

Compounds **1** and **2** were synthesized under similar conditions except for the use of phen in the preparation of **1** but not of **2**. However, **1** and **2** are of different structural types. The former is a chain while **2** displays a 3-D open framework. It is possible that the coordination ability and steric effect of the phen group are much larger than those of H_2O, resulting in th occurrence of this situation. This result clearly shows that auxiliary ligands, as well as bridging ligands, also play an important role in regulating the structures of synthesized compounds.

Preliminary magnetic studies of **1** and **2** show that the values of the effective magnetic moments μ_{eff} at room temperature are 4.50 μ_B and 4.53 μ_B per Co formula unit, respectively, while the spin-only magnetic moments are 3.87 μ_B with $S = 3/2$ and $g = 2.0$ $\{\mu_{eff} = g[s(s+1)]^{1/2}\mu_B\}$. The differences are due to additional orbital momentum. When the temperature was lowered, μ_{eff} gradually decreased from 4.50 μ_B and 4.53 μ_B at 300 K to 1.24 μ_B and 2.27 μ_B at 2.0 K for **1** and **2**, respectively. Both plots of $1/\chi_m$ vs. T obey the Curie−Weiss law $[\chi_m = C/(T - \theta)]$ at 5000 Oe with Weiss constants, $\theta_1 = -17.74$ K and $\theta_2 = -13.13$ K, and Curie constants, $C_1 = 2.668$ emu·mol^{-1}·K and $C_2 = 2.653$ emu·mol^{-1}·K for **1** and **2**, respectively, which indicates the occurrence of antiferromagnetic coupling between the Co^{II} atoms in **1** and **2**.

In conclusion, the reactivity of organic ligands under hydrothermal condition shows some differences from that under usual conditions, thus indicating that modification of organic ligands under hydrothermal conditions is very promising for the synthesis of useful new ligands. The work described herein once again provides strong evidence that a wide variety of new coordination polymers can be produced by hydrothermal generation of new bridging ligands in the presence of appropriate metal ions, although it remains a great challenge to develop this technique to a stage where a desired structure or crystal symmetry can be ensured.

Experimental Section

Syntheses of 1 and 2: Dark brown block crystals of **1** were synthesized hydrothermally from a mixture of $CoCl_2·6H_2O$, H_4bta, $N_2H_4·H_2O$, phen and H_2O (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 d and cooled to room temperature. The 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). Orange block crystals of **2** (yield 46% based on cobalt) were obtained under the same reaction conditions and experimental procedures as those for **1** using a molar ratio of $CoCl_2·6H_2O/H_4$bta/$N_2H_4·H_2O/H_2O$ = 2.6:5:4.5:625.

1: $[C_{22}H_{12}CoN_6O_4]_n$ (483.31): calcd. C 54.67, H 2.50, N 17.39; found C 54.81, H 2.79, N 17.01. IR (KBr disk, cm^{-1}): $\tilde{\nu}$ = 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.

2: $[C_{10}H_8CoN_4O_6]_n$ (339.13): calcd. C 35.42, H 2.38, N 16.52; found C 35.11, H 2.16, N 16.91. IR (KBr disk, cm^{-1}): $\tilde{\nu}$ = 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.

X-ray Crystallographic Studies

Compound 1: Dark brown block crystals, triclinic, space group $P\bar{1}$, a = 9.762(4), b = 10.169(4), c = 11.143 (4) Å, α = 80.96(3), β = 64.49(3), γ = 71.88(3)°, V = 948.4(7) Å^3, Z = 2, $D_{calcd.}$ = 1.692 g cm^{-3}, μ = 0.953 mm^{-1}. Data collections (4.06° ≤ 2θ ≤ 51.96°) were performed at 293(2) K with a Siemens P4 diffractometer (Mo-K_α, λ = 0.71073 Å). The structure was solved with direct methods and refined with full-matrix least squares (SHELXTL-97),[14] giving a final R_1 value of 0.0402 for 346 parameters and 3703 unique reflections with $I \geq 2\sigma(I)$ and wR_2 of 0.1040 for all 4533 reflections.

Compound 2: Orange block crystals, monoclinic, space group $P2_1/c$, a = 6.8687(5), b = 7.5943(6), c = 10.0401(6), β = 95.250(4)°, V = 521.52(6) Å^3, Z = 2, D_c = 2.160 g cm^{-3}, μ = 1.689 mm^{-1}. Data collections (5.96° ≤ 2θ ≤ 46.44°) were performed at 293(2) K with a Bruker-AXS Smart CCD diffractometer (Mo-K_α, λ = 0.71073 Å). The structure was solved with direct methods and refined with full-matrix least squares (SHELXTL-97), giving a final R_1 value of 0.0277 for 105 parameters and 751 unique reflections with $I \geq 2\sigma(I)$ and wR_2 of 0.0799 for all 2395 reflections.

CCDC-208867 (**1**) and -208868 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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