

The Structure and Fluorescence Properties of Two Novel Mixed-Ligand Supramolecular Frameworks with Different Structural Motifs

Zhi-Yong Fu,^[a,b] Xin-Tao Wu,^{*[a]} Jing-Cao Dai,^[a] Sheng-Min Hu,^[a] Wen-Xin Du,^[a] Han-Hui Zhang,^[c] and Rui-Qing Sun^[c]

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Two novel coordination polymers formed by cobalt nitrate and 1,2-bis(4-pyridyl)ethane with the homologous ligands 2-aminoterephthalic acid and terephthalic acid, respectively, have been prepared. One displays a fivefold diamond-type feature while the other exhibits a twofold interpenetrating

structural motif. The thermal and photoluminescence properties associated with their structures have been characterized and studied.

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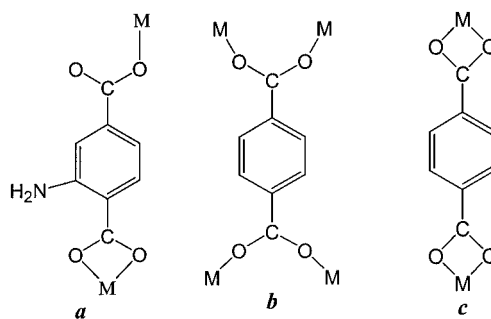
Introduction

The construction of functional metal-organic frameworks is of great interest due to their intriguing network topologies and their potential applications as microporous,^[1] magnetic,^[2] nonlinear optical^[3] and fluorescent materials.^[4] Molecular self-assembly has been proven as an effective way of constructing various fascinating supramolecular frameworks. The basic building blocks recognize each other in a reaction system and aggregate to form the bulk structure.^[5] Lots of supramolecular frameworks have already been produced in the past decade based upon the principle of crystal engineering.^[6] However, the mechanism of molecular self-assembly is unclear and the result of self-assembly is unpredictable, therefore an understanding of the factors that govern the assembly process is necessary for technological development. Recently, considerable attention has been focused on the influence of the factors involved in molecular self-assembly processes, such as the solvent system,^[7] template,^[8] counterion,^[9] and the conformational freedom of the ligands.^[10] We are particularly interested in self-assembly and the functionalities associated with different coordination conformations. Here, we report two novel mixed organic ligand supramolecular compounds [Co{1,2-bis(4-pyridyl)ethane}(2-aminoterephthalate)] (**1**) and [Co{1,2-bis(4-pyridyl)ethane}(terephthalate)] (**2**). The

O,O'-donor ligands adopt different coordination modes forming different kinds of building blocks, which finally aggregate to generate different supramolecular architectures, due to the influence of the substituent groups. These different structures show similar fluorescence spectra: they both display strong fluorescence emission at 400 nm.

Results and Discussion

2-Aminoterephthalic acid and terephthalic acid were chosen as starting materials as one has a substituted amino group while the other has none. These two organic acids react with 1,2-bis(4-pyridyl)ethane and cobalt nitrate in a 1:1:1 ratio under the same conditions. The O-donors accept different coordination modes (Scheme 1), which finally results in different coordination frameworks.



Scheme 1. The coordination modes of the carboxylate group: a) unidentate and chelating bis-bidentate; b) bidentate; c) chelating bidentate

^[a] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China
Fax: (internat.) +86-591/371-4946
E-mail: wxt@ms.fjirsm.ac.cn

^[b] Graduate School of the Chinese Academy of Sciences
Fuzhou, Fujian 350002, China

^[c] Department of Chemistry, Fuzhou University
Fuzhou, Fujian 350002, China

Crystal Structures

An ORTEP view of a Co center of compound **1** is shown in Figure 1. The Co atom has a distorted tetrahedral coordination geometry, being coordinated by two N atoms of two 1,2-bis(4-pyridyl)ethane molecules [$\text{Co1-N2b} = 2.101(11)$ Å, $\text{Co1-N3} = 2.063(11)$ Å], two O atoms from one chelating bis-bidentate carboxylate group [$\text{Co1-O1a} = 2.050(10)$ Å, $\text{Co1-O2a} = 2.224(10)$ Å], and one O atom of one unidentate carboxylate group [$\text{Co1-O3} = 2.024(9)$ Å], which provide the four connecting nodes resulting in an unsymmetrical adamantane-type unit (Figure 2). No guest

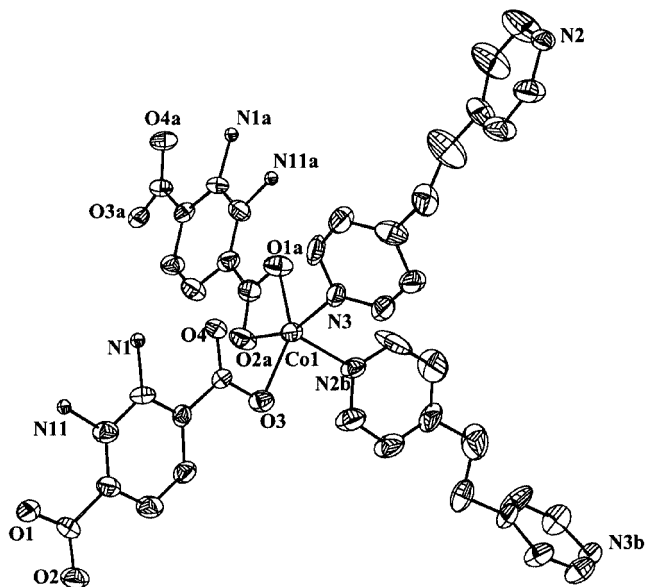


Figure 1. ORTEP drawing of **1** around the Co center (ellipsoids at 30% probability); the hydrogen atoms are omitted for clarity; the N1 and N11 atoms of compound **1** were located from the E-map directly, and the displacement parameters of them were of 0.5 to 0.5 statistically; symmetry codes: $a = -x, 1 + y, z - 1/4$; $b = x, 2 - y, z + 1/4$

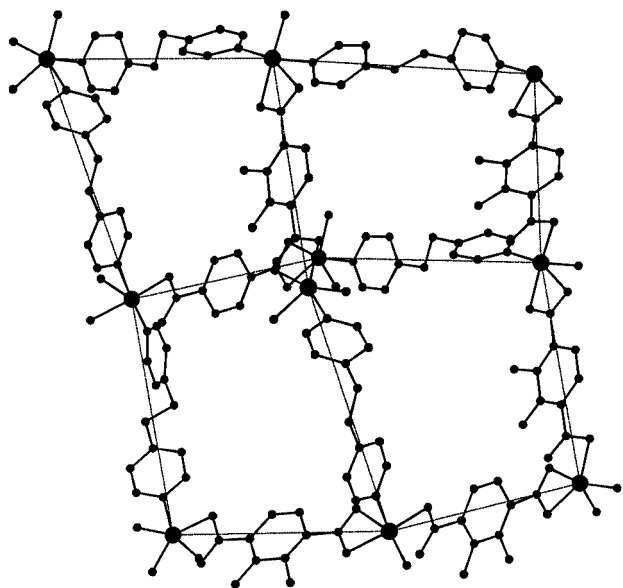


Figure 2. View of the adamantane units of **2**; the large black balls represent the Co atoms

molecules were found in the cage of the adamantane unit and distortions of the unit can arise from the application of different ligands. Four 2-aminoterephthalate ligands and two 1,2-bis(4-pyridyl)ethane ligands bridge six Co atoms to form a hexagonal circuit. The distance between the Co centers is determined by the length of 2-aminoterephthalate (10.729 Å) or 1,2-bis(4-pyridyl)ethane (13.349 Å). Figure 3 shows that five independent equivalent networks are interpenetrated within the structure (fivefold diamondoid mode). The nodes of four other nets are arranged between the top-most and bottom-most extremities of an adamantane unit of the first net. Although many diamond-related nets displaying various interpenetration modes ranging from two- to ninefold have been reported,^[13] the fivefold interpenetration of **1** is novel in the presence of the mixed organic ligands with different lengths. To the best of our knowledge, with coordination polymers only two other examples of a fivefold diamond-type net have been previously observed. They are $[\text{Cu}(\text{L}_2)](\text{BF}_4)$ ($\text{L} = 1,4\text{-dicyanobenzene}$) and $[\text{Cu}(\text{bpe})_2](\text{BF}_4)$ generated by the reaction of CuBF_4 with 1,4-dicyanobenzene and bpe, respectively.^[14]

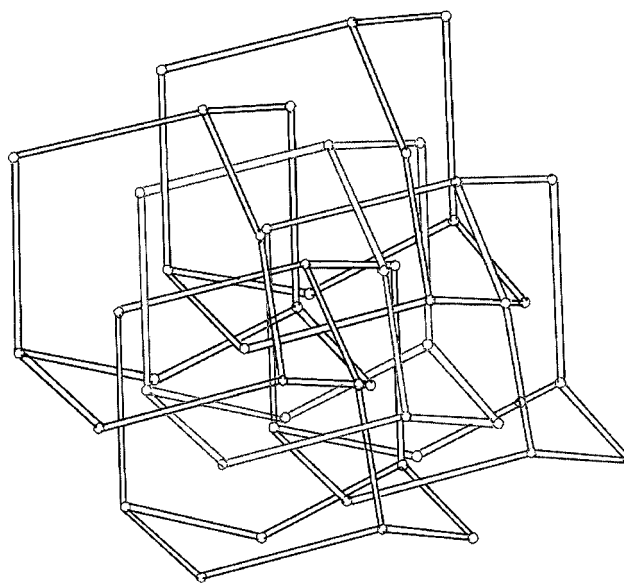


Figure 3. The interpenetration model for complex **1**

For the preparation of compound **2**, the terephthalate ligand was used instead of 2-aminoterephthalate ligand. The Co center has a distorted octahedral coordination geometry, with two oxygen donors of one chelating bis-bidentate carboxylate group [$\text{Co1-O1} = 2.200(3)$ Å, $\text{Co1-O2} = 2.192(3)$ Å] and two oxygen donors of two bridging bidentate carboxylate groups in the horizontal direction ($\text{Co1-O3} = 2.017$ Å, $\text{Co1-O4a} = 2.028$ Å). The coordination sphere is completed by two nitrogen donors of 1,2-bis(4-pyridyl)ethane [$\text{Co1-N1} = 2.163(3)$ Å, $\text{Co1-N2b} =$

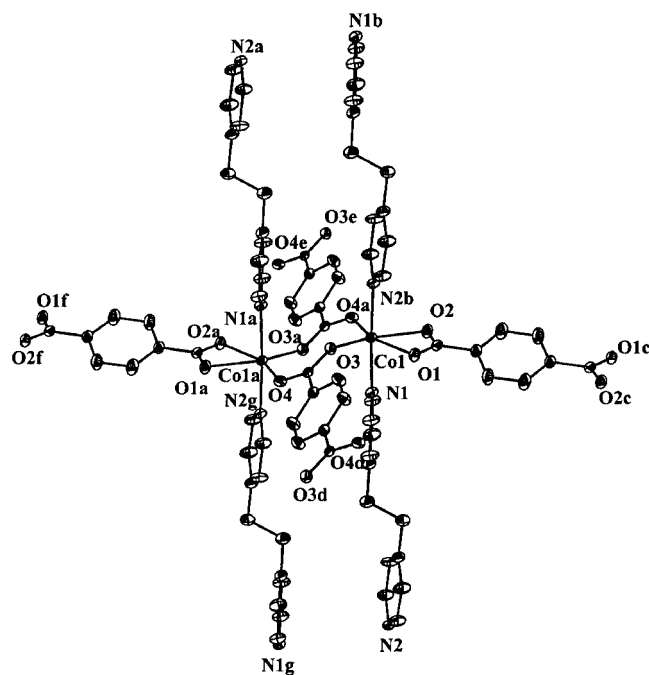


Figure 4. View of the dimetal unit of **2**; hydrogen atoms have been omitted, and the ellipsoids at 30% probability represent C, N, O, and Co; symmetry codes: $a = -x, -y, -z$; $b = x, y + 1, z - 1$; $c = 1 - x, -1 - y, -1 - z$; $d = 1 - x, -y, -z$; $e = -1 + x, y, z$; $f = -1 + x, 1 + y, 1 + z$; $g = -x, -1 - y, 1 - z$.

2.152(3) Å] in the axial direction (Figure 4). The coordination mode in compound **2** generates a novel cuboidal building block (Figure 5). Each corner of the cuboidal block is occupied by a binuclear subunit and the Co...Co separation in the binuclear subunit is 4.27 Å. Eight terephthalate ligands form the length and width of the cuboidal block while eight 1,2-bis(4-pyridyl)ethane ligands make up the height of it. No guest molecule is included in the cuboidal

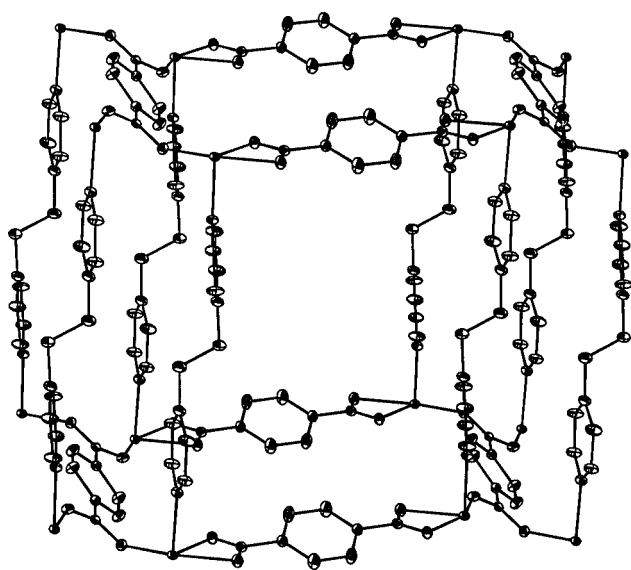


Figure 5. Structure of the cuboidal block of **2**, showing eight Co₂ units linked by eight terephthalate anions and eight 1,2-bis(4-pyridyl)ethane units.

box. The aggregation of the building blocks results in a 3-D framework, and the 3-D networks interlock with each other displaying a twofold-interpenetrating mode. As shown in Figure 6, in the axial direction every two rods (rod a and b) in the cuboidal block are associated with one particular quadrate ring (ring 1) of the other framework through which they pass, while in the horizontal direction one rod (rod c) is associated with two particular quadrate rings (ring 2 and 3) of the other framework through which it penetrates.

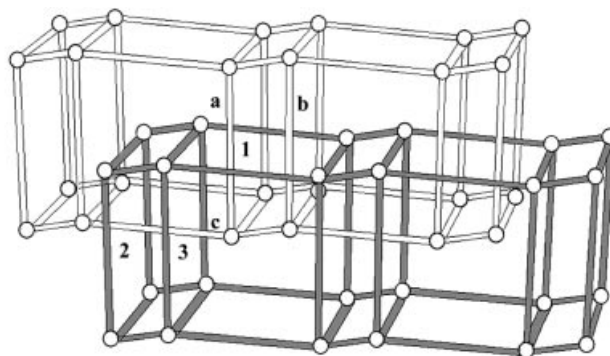


Figure 6. The interpenetration model for complex **2**.

Under the same reaction conditions, compounds **1** and **2** exhibit different structural motifs. The coordination mode of the carboxylate group is an essential factor in affecting the bulk structures of **1** and **2**. One of the characteristics of these reactions is that the substituent groups in the homologous O,O'-donor ligands are slightly different, which affects the pH values in the reaction systems (obsd. 6.22 in **1** and 5.13 in **2**). These different basicities, which most probably make the carboxylate groups in **1** and **2** accept different coordination modes, lead to different supramolecular architectures.

IR Spectroscopy

The IR spectrum of compound **1** shows the characteristic bands of the dicarboxylate groups of the 2-aminoterephthalate ligands at 1618–1549 cm⁻¹ for the asymmetric vibration and at 1421–1396 cm⁻¹ for the symmetric vibration. While the IR spectrum of compound **2** shows the characteristic bands of the dicarboxylate groups of the terephthalate ligands at 1610–1552 cm⁻¹ for the asymmetric vibration and at 1410–1394 cm⁻¹ for the symmetric vibration. The splitting of $\nu_{\text{asym}}(\text{CO}_2)$ in compound **1** and compound **2** confirms that the carboxylate groups have two different coordination modes,^[15] in agreement with their crystal structures. The absence of the expected characteristic bands at 1730–1690 cm⁻¹ for the protonated carboxylate groups indicates the complete deprotonation of 2-aminoterephthalic acid and terephthalic acid in the reaction with Co ions.^[16]

Thermal and Fluorescent Properties

Compounds **1** and **2** were heated to 600 °C under N₂. Their thermal decomposition behavior (Figure 7) is very similar. No obvious decomposition was observed until ca 430 °C. The TGA data show that **1** has an obvious weight loss starting at about 435 °C (437 °C for **2**).

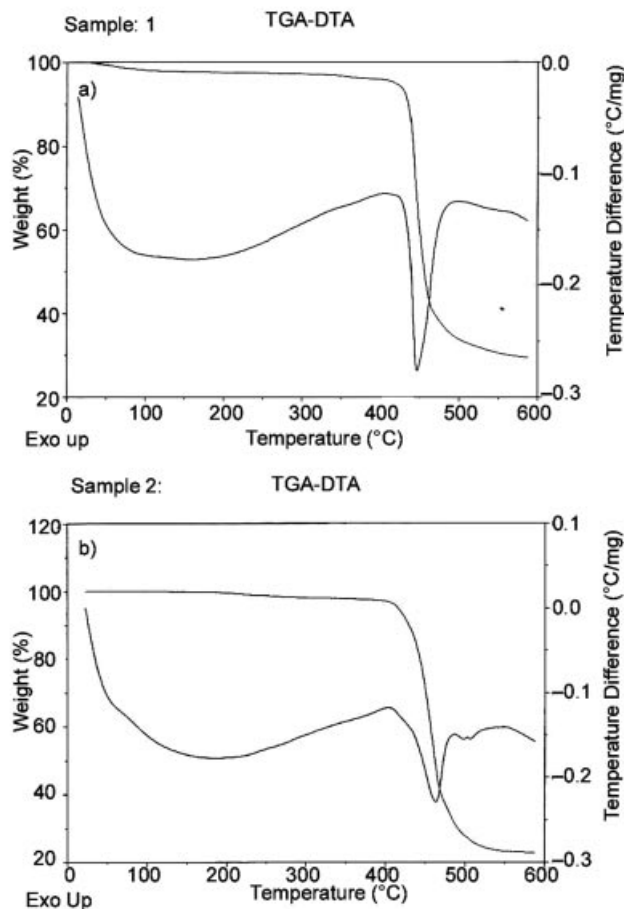


Figure 7. The TGA-DTA diagram for the coordination polymers: a) compound **1**; b) compound **2**

The emission spectra of compounds **1** and **2** in the solid state at room temperature are shown in Figure 8. It can be seen that **1** exhibits an intense photoluminescence emission at 400 nm (Figure 8a, $\lambda_{\text{ex}} = 300$ nm) while **2** also exhibits an intense photoluminescence emission at 400 nm (Figure 8b, $\lambda_{\text{ex}} = 310$ nm). These emissions may be assigned as ligand-to-metal charge transfer (LMCT).^[17] Due to their high thermal stability, **1** and **2** may be good candidates for emitting diode devices.

It is very interesting to note that **1** and **2** exhibit similar thermal behaviors and photoluminescence spectra despite having different structural motifs. What is the reason for these phenomena? Due to the fact that thermal behaviors and photoluminescence behavior are closely associated with the metal ions and the ligands coordinated around them, we decided to look again at the coordination environments of the metal ions in **1** and **2**. In **1** the Co atom has a distorted tetrahedral coordination geometry while in **2** the Co

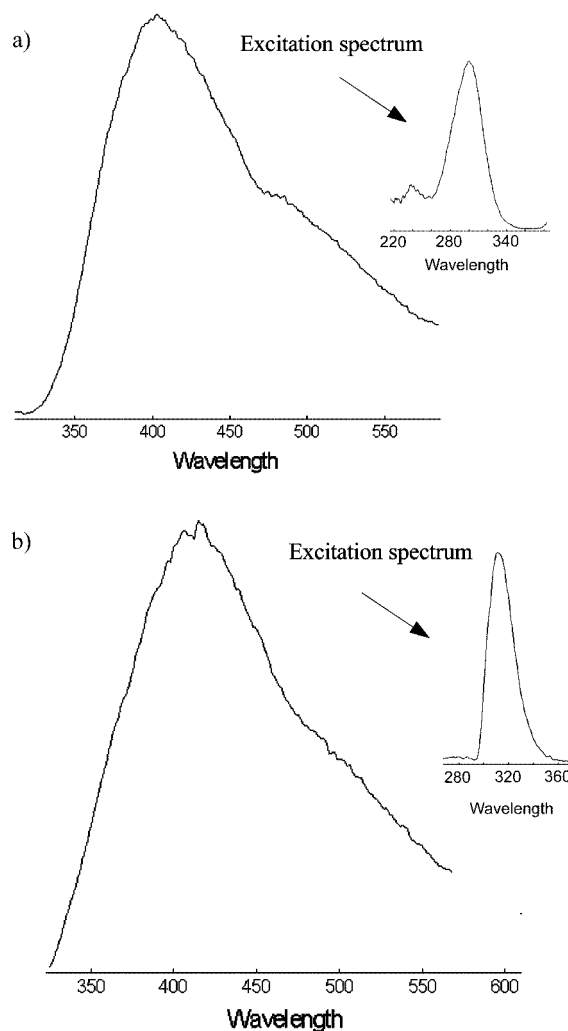


Figure 8. Solid-state emission spectra of the coordination polymers at room temperature: a) compound **1**; b) compound **2**

atom has a distorted octahedral coordination geometry. However, despite this distinct disparity, the ligands coordinated around the metal ions in **1** and **2** are similar (Figure 1 and Figure 4). The Co center in **1** has one chelating bis-bidentate carboxylate group, one unidentate carboxylate group, and two 1,2-bis(4-pyridyl)ethane ligands while in **2** there are one chelating bis-bidentate carboxylate group, two bridging bidentate carboxylate groups, and two 1,2-bis(4-pyridyl)ethane ligands. These similar environments may be the reason for the similar thermal and photoluminescence behaviors (Figure 7 and 8).

Conclusion

Two novel coordination polymers formed by cobalt nitrate and 1,2-bis(4-pyridyl)ethane with the homologous ligands 2-aminoterephthalic acid and terephthalic acid have been prepared and characterized. Compound **1** displays a fivefold diamond-type net while compound **2** exhibits a twofold-interpenetrating structural motif. The two com-

pounds have similar thermal behaviors and photoluminescence spectra. In this paper, we have shown that the amino group in 2-aminoterephthalic acid plays an important role in affecting the coordination mode of the carboxylate group, causing **1** to have a structural motif that is clearly different from that of **2**. Their thermal and photoluminescence properties are closely associated with the coordination environments around the metal centers.

Experimental Section

General Remarks: All reactions were carried out in hydrothermal conditions. All chemicals are commercially available and used as received without further purification. The C, H and N microanalyses were carried out with a Vario EL III elemental analyzer. Infrared spectra (KBr pellets) were recorded in the range from 4000–400 cm^{-1} on a Nicolet Magna 750 FT-IR spectrometer. Thermogravimetric analyses (TGA) were performed under nitrogen with a heating rate of 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$ using a TA5200/MDSC2910 system. Fluorescent spectra were measured with an Edinburgh FL-FS90 TCSPC system at the Spectroscopy Lab of Fuzhou University.

Synthesis of [Co{1,2-bis(4-pyridyl)ethane}(2-aminoterephthalate)] (1): An aqueous mixture (10 cm^3) containing $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.292 g, 1 mmol), 1,2-bis(4-pyridyl)ethane (0.184 g, 1 mmol), 2-aminoterephthalic acid (0.181 g, 1 mmol) and NaOMe (0.108 g, 2 mmol) was placed in a Parr Teflon-lined stainless steel bomb (25 cm^3). The bomb was heated at 5 $^{\circ}\text{C}\cdot\text{min}^{-1}$ to 160 $^{\circ}\text{C}$; after 24 h at 160 $^{\circ}\text{C}$ it was cooled to 90 $^{\circ}\text{C}$ at the rate of 0.1 $^{\circ}\text{C}\cdot\text{min}^{-1}$, then maintained at that temperature for 12 h. Finally, it was cooled at 0.1 $^{\circ}\text{C}\cdot\text{min}^{-1}$ to 20 $^{\circ}\text{C}$. The bomb was opened to give red block crystals in 62% yield. $\text{C}_{20}\text{H}_{17}\text{CoN}_3\text{O}_4$ (422.3): calcd. C 56.86, H 4.06, N 9.95; found C 56.96, H 4.01, N 9.97. IR (KBr): $\tilde{\nu}$ = 3442m, 3338m, 3055w, 2945w, 1618s, 1564s, 1549s, 1498m, 1446m, 1421s, 1396s, 1375m, 1333w, 1261s, 1072w, 1028s, 847s, 816m, 768s, 702w, 536w, 517w cm^{-1} .

Table 1. Crystal data and refinement details for the structures of **1** and **2**

Complex	1	2
Empirical formula	$\text{C}_{20}\text{H}_{17}\text{CoN}_3\text{O}_4$	$\text{C}_{20}\text{H}_{16}\text{CoN}_2\text{O}_4$
Space group	$P4_1$	$P\bar{1}$
<i>a</i> , Å	9.1737(4)	10.0719(3)
<i>b</i> , Å	9.1737(4)	10.23420(10)
<i>c</i> , Å	24.6489(16)	10.8551(3)
α	90 $^{\circ}$	80.34 $^{\circ}$
β	90 $^{\circ}$	66.6430(10) $^{\circ}$
γ	90 $^{\circ}$	75.474(2) $^{\circ}$
<i>V</i> , Å ³	2074.37(19)	991.45(4)
<i>Z</i>	4	2
$\mu(\text{Mo}-K_{\alpha})$, mm^{-1}	0.856	0.891
<i>d</i> _{calcd.} , g/cm^3	1.352	1.364
Measured reflections	5098	5139
Independent reflections	2051	3450
Observed reflections	1247	2612
$[I > 2\sigma(I)]$		
R	0.0790	0.0502
wR	0.1465	0.1145
Max/mean shift in final cycle	0.000/0.000	0.000/0.000

Synthesis of [Co{1,2-bis(4-pyridyl)ethane}(terephthalate)] (2): An aqueous mixture (10 cm^3) containing $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.292 g, 1 mmol), 1,2-bis(4-pyridyl)ethane (0.184 g, 1 mmol), terephthalic acid (0.166 g, 1 mmol) and NaOMe (0.108 g, 2 mmol) was placed in a Parr Teflon-lined stainless steel bomb (25 cm^3). The bomb was heated at 5 $^{\circ}\text{C}\cdot\text{min}^{-1}$ to 160 $^{\circ}\text{C}$; after 24 h at 160 $^{\circ}\text{C}$ it was cooled to 90 $^{\circ}\text{C}$ at the rate of 0.1 $^{\circ}\text{C}\cdot\text{min}^{-1}$, then maintained at that temperature for 12 h. Finally, it was cooled at 0.1 $^{\circ}\text{C}\cdot\text{min}^{-1}$ to 20 $^{\circ}\text{C}$. The bomb was opened to give red block crystals in 75% yield. $\text{C}_{20}\text{H}_{16}\text{CoN}_2\text{O}_4$ (407.3): calcd. C 58.98, H 3.96, N 6.88; found C 58.87, H 3.92, N 6.89. IR (KBr): $\tilde{\nu}$ = 3057w, 2933w, 1610s, 1568s, 1552s, 1510m, 1500m, 1427m, 1410s, 1394s, 1306w, 1221w, 1018m, 841s, 818m, 748s, 550s, 523m cm^{-1} .

X-ray Crystallographic Study: Crystallographic data for compound **1** and compound **2** are listed in Table 1. For compound **1**, a red block crystal with dimensions of 0.40 $\times$ 0.14 $\times$ 0.14 mm was used. For compound **2**, a red block crystal with dimensions of 0.30 $\times$ 0.22 $\times$ 0.12 mm was used. Data for **1** and **2** were collected at room temperature on a Siemens SMART-CCD area-detector diffractometer with Mo- K_{α} radiation (λ = 0.71073 Å) and a graphite monochromator using the ω -scan mode. Data reductions and absorption corrections were performed with SMART and SADABS software, respectively. For all structural analyses, all calculations were performed on an indy workstation from Silicon Graphics with the program SHELXTL.^[11] The structures were solved by direct methods. The refinement of structures was performed by full-matrix least-squares techniques on F^2 using SHELXL-97.^[12] All non-hydrogen atoms were treated anisotropically. The nitrogen atoms of 2-aminoterephthalate exhibit disorder. They were located from

Table 2. Selected bond lengths (Å) and bond angles (deg) for **1** and **2**

[Co{1,2-bis(4-pyridyl)ethane}(2-aminoterephthalate)] (1) ^[a]			
Co(1)–O(3)	2.024(9)	N(2)–Co(1c)	2.101(11)
Co(1)–O(1a)	2.050(10)	O(2)–Co(1d)	2.224(10)
Co(1)–N(3)	2.063(11)	O(1)–Co(1d)	2.050(10)
Co(1)–N(2b)	2.101(11)	Co(1)–O(4)	2.347(9)
Co(1)–O(2a)	2.224(10)		
O(3)–Co(1)–O(1a)	147.2(4)	N(3)–Co(1)–O(2a)	157.9(4)
O(3)–Co(1)–N(3)	106.5(4)	N(2b)–Co(1)–O(2a)	88.6(4)
O(1a)–Co(1)–N(3)	97.7(4)	O(3)–Co(1)–O(4)	60.0(4)
O(3)–Co(1)–N(2b)	96.9(4)	O(1a)–Co(1)–O(4)	99.2(4)
O(1a)–Co(1)–N(2b)	101.2(4)	N(3)–Co(1)–O(4)	89.6(4)
N(3)–Co(1)–N(2b)	98.5(5)	N(2b)–Co(1)–O(4)	156.9(4)
O(3)–Co(1)–O(2a)	93.4(4)	O(2a)–Co(1)–O(4)	92.1(4)
O(1a)–Co(1)–O(2a)	60.3(4)		
[Co{1,2-bis(4-pyridyl)ethane}(terephthalate)] (2) ^[b]			
Co(1)–O(3)	2.017(3)	Co(1)–O(2)	2.192(3)
Co(1)–O(4a)	2.028(3)	Co(1)–O(1)	2.200(3)
Co(1)–N(2b)	2.152(3)	O(4)–Co(1a)	2.028(3)
Co(1)–N(1)	2.163(3)	N(2b)–Co(1)–O(2)	90.90(11)
O(3)–Co(1)–O(4a)	110.08(11)	N(1)–Co(1)–O(2)	85.36(11)
O(3)–Co(1)–N(2b)	88.43(12)	O(3)–Co(1)–O(1)	155.72(11)
O(4a)–Co(1)–N(2b)	89.31(11)	O(4a)–Co(1)–O(1)	93.97(11)
O(3)–Co(1)–N(1)	92.04(12)	N(2b)–Co(1)–O(1)	88.58(12)
O(4a)–Co(1)–N(1)	94.00(11)	N(1)–Co(1)–O(1)	89.47(12)
N(2b)–Co(1)–N(1)	176.26(12)	O(2)–Co(1)–O(1)	60.01(10)
O(3)–Co(1)–O(2)	95.95(10)	O(4a)–Co(1)–O(2)	153.96(11)

^[a] Symmetry codes: (a) $-x, y + 1, z - 1/4$; (b) $x, 2 - y, z + 1/4$; (c) $-x + 2, y, z - 1/4$; (d) $x - 1, -y, z + 1/4$. ^[b] Symmetry codes: (a) $-x, -y, -z$; (b) $x, y + 1, z - 1$

the E-map directly, and the displacement parameters were of 0.5 to 0.5 statistically. The positions of the hydrogen atoms were generated geometrically. Selected bond lengths and bond angles for the cluster cores of **1** and **2** are listed in Table 2.

CCDC-181331 (**1**) and -181332 (**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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