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Construction of Metal-Organic Frameworks with the Pyridine-3,5-dicarboxylate Anion and Bis(imidazole) Ligands: Synthesis, Structure, and Thermostability Studies

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Three novel metal-organic polymers, namely, $[Ni(L^1)_{0.5}(3,5\text{-pdc})(\mu\text{-}H_2O)]\cdot H_2O$ (**1**), $[Co(L^2)(3,5\text{-pdc})]\cdot 2H_2O$ (**2**), and $[Co(L^3)(3,5\text{-pdc})(\mu\text{-}H_2O)]\cdot H_2O$ (**3**) [3,5-pdc = pyridine-3,5-dicarboxylate, L^1 = 1,4-bis(imidazol-1-ylmethyl)benzene, L^2 = 1,1′-(1,4-butanediyl)bis(imidazole), and L^3 = 1,1′-(1,4-hexanediyl)bis(imidazole)], have been hydrothermally synthesized and characterized by single-crystal X-ray diffraction (XRD), thermogravimetric (TG) analysis, and elemental analysis (EA). Polymers **1** and **2** have the identical 2D [M(3,5-pdc)] sheet skeleton, however, different bis(imidazole) ligands cause **1** to have a 2D (3,4)-connected double-layer net featuring the $(6^3)(6^4\cdot 8^2)$ topology symbol and **2** to have a 2D (3,5)-connected net characterized by the $(3\ 5^2)(3^2\cdot 5^3\cdot 6^4\cdot 7)$ topology symbol. They are both extended to 3D supramolecular frameworks through the O–H···O hydrogen bonds. In particular, in **2** there exists a four-membered Z-shape water cluster. The Co ions in **3** are connected by 3,5-pdc and L^3 to give rise to a complicated 3D framework that can be described as a (3,5)-connected $(4^2\cdot 5)(4^2\cdot 6^3\cdot 8^2\cdot 10^2\cdot 12)$ network. In addition, the thermal analysis of these three complexes has been measured and discussed.

Introduction

The construction of metal-organic frameworks (MOFs) is receiving increasing attention because of the potential applications of these novel functional materials as molecular sieves and in the areas of magnetism, gas storage, size- and shape-selective catalysis, and electrical conductivity.[1] The art of creating different superstructures by assembling similar components has met with great success, especially with nitrogen- and oxygen-containing ligands capable of metal coordination. The control of the molecular geometry has yielded promising results for assembling new and robust higher-order molecular architectures.[2]

To date, a large number of MOFs based on flexible bis(imidazole) ligands have been constructed.[3] Such ligand bearing alkyl spacers are a good choice for a N-donor ligand. The flexible nature of the spacers allows the ligands to bend and rotate when they coordinate to the metal centers, and this often causes the structural diversity. In the literature, the counteranions focus on inorganic anions (such as N_3^-, SCN^-, and CN^-)[4] and carboxylate-containing ligands (such as 1,4-benzenedicarboxylate, 1,3,5-benzenetricarboxylate, 1,2,4,5-benzenetetracarboxylate, and methylenediisophthalic acid).[5–7] In contrast, the N-donor aromatic multicarboxylate ligands, pyridine-2,3-dicarboxylic acid (2,3-pdc), pyridine-2,6-dicarboxylic acid (2,6-pdc), and pyridine-2,5-dicarboxylic acid (2,5-pdc), have rarely been reported.[8–10] To the best of our knowledge, pyridine-3,5-dicarboxylate (3,5-pdc) has not been reported as the counteranion. Therefore, we chose pyridine-3,5-dicarboxylate (3,5-pdc) as the organic counteranion and three bis(imidazole)-containing ligands, 1,4-bis(imidazol-1-ylmethyl)benzene (L^1), 1,1′-(1,4-butanediyl)bis(imidazole) (L^2), and 1,1′-(1,4-hexanediyl)bis(imidazole) (L^3), as the neutral ligands to combine with the metal ions. Fortunately, three new compounds, namely, $[Ni(L^1)_{0.5}(3,5\text{-pdc})(\mu\text{-}H_2O)]\cdot H_2O$ (**1**), $[Co(L^2)(3,5\text{-pdc})]\cdot 2H_2O$ (**2**), and $[Co(L^3)(3,5\text{-pdc})(\mu\text{-}H_2O)]\cdot H_2O$ (**3**), were successfully obtained and characterized by single-crystal X-ray diffraction (XRD), infrared (IR) spectroscopy, and elemental analysis (EA). In addition, the thermogravimetric analysis of these complexes is discussed in detail.

Results and Discussion

Description of the Crystal Structures

$[Ni(L^1)_{0.5}(3,5\text{-pdc})(\mu\text{-}H_2O)]\cdot H_2O$ (1)

The single-crystal X-ray diffraction analysis revealed that the asymmetrical unit of complex **1** contains one Ni atom, one 3,5-pdc anion, half a L^1 ligand, one coordinated water molecule, and one free water molecule. Each Ni atom is five-coordinate and is coordinated to two O atoms from two 3,5-pdc anions (Ni–O 2.050–2.069 Å), one N atom

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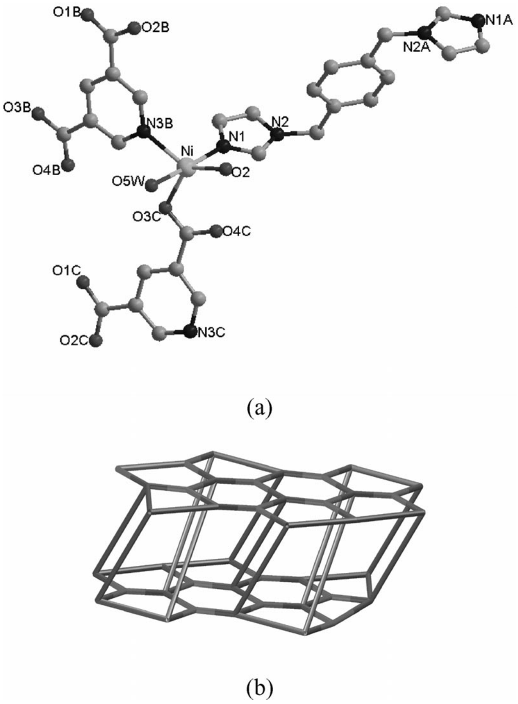
from one L^1 ligand (Ni–N 2.081 Å), one N atom from one 3,5-pdc anion (Ni–N 2.135 Å), and one water molecule (Ni–O 2.100 Å) to give the NiO_3N_2 trigonal bipyramidal geometry, as shown in Figure 1 (a). The Ni–O/N bond lengths are comparable to other related Ni-based complexes.[11] Each 3,5-pdc anion in **1** coordinates to three Ni atoms to afford a 2D sheet (see Figure S1 in the Supporting Information). Two adjacent 2D sheets are linked in a *trans* fashion by the L^1 ligands to generate a double-layer net, as shown in Figure 1 (b). If the metal centers and the 3,5-pdc anions are viewed as the 4- and 3-connected nodes, respectively, then this double-layer net exhibits (3,4)-connection with $(6^3)(6^4{\cdot}8^2)$ topology. Interestingly, some free water molecules are stored in the solvent-accessible void space of the double-layer net, which are stabilized by typical O–H···O hydrogen bonds (O6–H6B···O1 2.926 Å and O6–H5A···O4 2.851 Å). Furthermore, the double-layer net framework is extended to a 3D supramolecular framework through the O–H···O hydrogen bonds between the 2D nets (O5–H5B···O1 2.823 Å and O5–H5A···O4 2.770 Å).



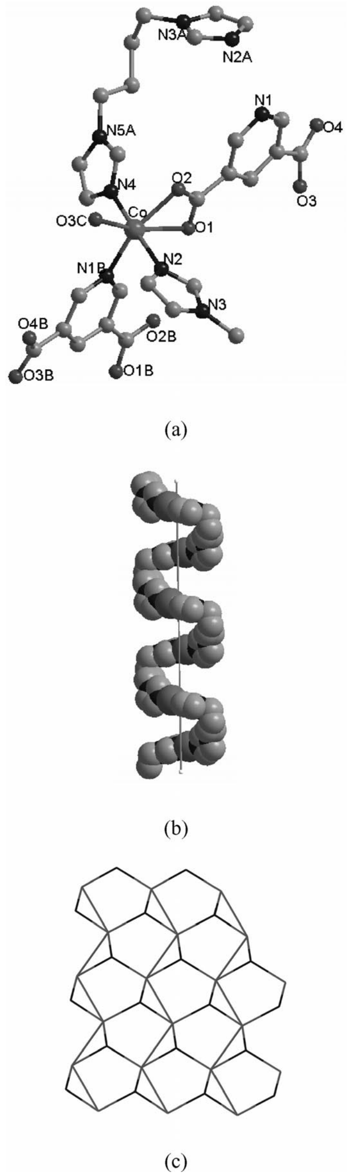
(a)

(b)

Figure 1. (a) The coordination environments for the Ni atoms in **1**. All hydrogen atoms are omitted for clarity. (b) The schematic description of the (3,4)-connected 2D net.

[Co(L^2)(3,5-pdc)]·2H_2O (2)

Single-crystal X-ray diffraction analysis showed that the asymmetrical unit of complex **2** contains one Co atom, one 3,5-pdc anion, one L^2 ligand, and two free water molecules. The six-coordinate Co ions are ligated to three O atoms from two 3,5-pdc anions (Co–O 2.052–2.325 Å), one N atom from one 3,5-pdc anion (Co–N 2.079 Å), and two N atoms from two L^2 ligands (Co–N 2.072–2.075 Å) resulting in the distorted octahedral geometry (Figure 2, a). The Co–O/N bond lengths are comparable to other related Co-based complexes.[12] As in compound **1**, each 3,5-pdc anion coordinates to three Co ions to form a 2D layer. The L^2 ligands display a *cis* configuration with a dihedral angle of 68.42° between the two imidazole rings in the L^2 ligand. As shown in Figure 2 (b), the arrangement of the Co^{II} atoms and the L^2 ligands gives a 1D $[Co(L^2)]_n$ helical chain along the *a* direction. The 2D [Co(3,5-pdc)] layer is decorated with these helical chains. Topological analysis reveals that it is a 2D (3,5)-connected net with $(3\ 5^2)(3^2{\cdot}5^3{\cdot}6^4{\cdot}7)$ topology, where the metal centers and the 3,5-pdc ligands act as the 5- and 3-connected nodes, respectively (Figure 2, c). Furthermore, the double-layer net framework is extended to a 3D supramolecular framework through the O–H···O



(a)

(b)

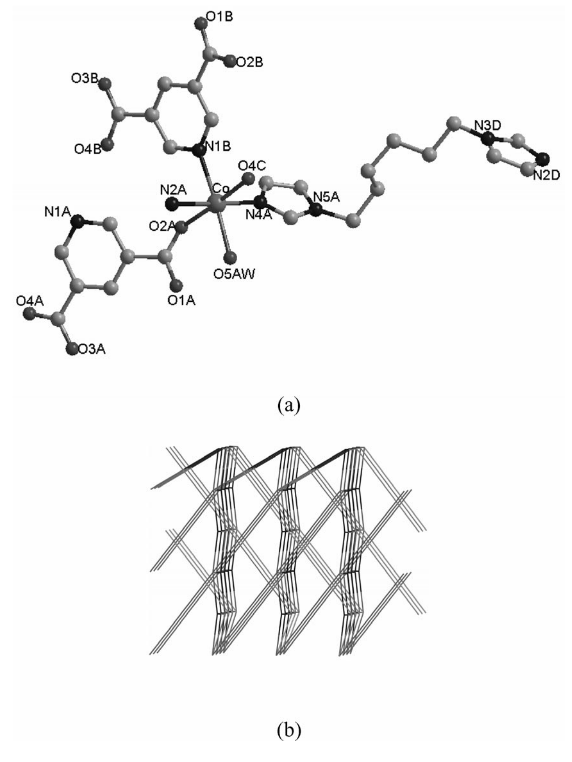
(c)

Figure 2. (a) The coordination environments for the Co atoms in **2**. All hydrogen atoms are omitted for clarity. (b) View of the 1D $[Co(L^2)]_n$ helical chain. (c) The topological representation of the 2D sheet.

hydrogen bonds between the 2D nets (O6–H6A···O5 2.731 Å, O6–H6B···O6 3.040 Å, O5–H5A···O1 2.780 Å, and O5–H5B···O4 2.721 Å).

[Co(L^3)(3,5-pdc)(μ-H_2O)]·H_2O (3)

Part of the structure for compound **3** is shown in Figure 3 (a). Single-crystal X-ray diffraction analysis showed that the asymmetrical unit of compound **3** contains one Co atom, one 3,5-pdc anion, one L^3 ligand, one coordinated water molecule, and one free water molecule. Each Co atom is coordinated to two O atoms from two 3,5-pdc anions [Co–O 2.110(4)–2.160(2) Å], two N atoms from two L^3 ligands [Co–N 2.086(4)–2.133(2) Å], one N atom from one 3,5-pdc ligand (Co–N 2.220 Å), and one water molecule (Co–O 2.144 Å) to give the CoO_3N_3 distorted octahedron geometry. The Co–O/N bond lengths are comparable to the aforementioned Co–O/N bond lengths in polymer **2**. Each 3,5-pdc anion coordinates to three Co centers to generate a 1D ladder-like chain instead of a 2D sheet (see Figure S2 in the Supporting Information). The L^3 ligands display *trans* configuration with a dihedral angle of 9.46° between the two imidazole rings in the L^3 ligand. Furthermore, the Co ions are connected by the 3,5-pdc anions and the L^3 ligands to give rise to a complicated 3D framework where the void space is occupied by free water molecules, which are stabilized by typical O–H···O hydrogen bonds (O5–H5A···O1 2.704 Å, O5–H5B···O6 2.685 Å, O6–H6A···O5 2.818 Å, and O6–H6B···O3 2.705 Å). The overall structure is a binodal (3,5)-connected $(4^2·5)(4^2·6^3·8^2·10^2·12)$ network (Figure 3, b). Although the (3,5)-connected frameworks are often encountered in the literature,[13] we are not aware of another compound characterized by the topology of **3**.



(a)

(b)

Figure 3. (a) The coordination environments for the Co atoms in **3**. All hydrogen atoms are omitted for clarity. (b) The topological representation of the 3D (3,5)-connected network.

TG Analysis

In order to estimate the stability of the coordination architectures, TG analysis experiments were carried out. Polymers **1** and **3** lost the free and coordinated water molecules at 50–190 °C (calcd. 9.5%; found 9.3%) and at 70–140 °C (calcd. 7.5%; found 7.4%), respectively, while compound **2** released the free water molecules in the room temperature to 200 °C range (calcd. 8.0%; found 8.4%). The mass of these polymers remains constant to about 330 °C for **1**, 340 °C for **2**, and 300 °C for **3** (see Figure S3 in the Supporting Information).

Conclusions

In summary, using the N-containing dicarboxylate ligand 3,5-pdc in the presence of the flexible bis(imidazole) ligands L^1, L^2, and L^3 we have assembled three novel coordination polymers with different topological structures. Through comparison between the structures of **1**–**3**, it was evident that the coordination modes of the 3,5-pdc anion play a significant role in determining the final metal-organic framework. Superficially, the 3,5-pdc anions in compounds **1** and **3** seem to adopt the same coordination mode and they both connect three metal ions with two monodentate carboxylates and one N atom. However, closer inspection reveals their differences, namely, that in **1** one of the carboxylate O atoms that participates in coordination is close to the N atom while the other is not, whereas in **3**, both O atoms are close to the N atom. This causes the formation of the 2D [Ni(3,5-pdc)] sheet for **1** and the 1D [Co(3,5-pdc)] ladder-like chain for **3**. In compound **2**, one carboxylate group of the 3,5-pdc anions adopts the chelated coordination mode, which is similar to the one close to the N atom in **1**. Consequently in **2** the identical 2D [Co(3,5-pdc)] sheet is obtained. However, the connectivity within the three compounds is also strongly related to the structural differences of the three bis(imidazole) ligands. The structure and the properties of compounds are often modified by changing the spacer groups. For compounds **1** and **2** there exists the same 2D [M(3,5-pdc)] (M = Ni, Co) sheet. The *trans* L^1 ligand acts as a connector that links two 2D sheets together to form a double-layer network, while the *cis* L^2 ligand combines with the metal ions to afford a 1D helical chain decorating the 2D sheet. This may be because the L^1 ligand is more rigid than L^2 due to the presence of the aromatic ring. In addition, the hydrogen bonding interactions both stabilize the ultimate structure and further extend the 2D sheet into the 3D supramolecular framework. This work demonstrates once again the aesthetic diversity of coordination chemistry and provides motivation to assemble more novel compounds with interesting structures and useful physical properties.

Experimental Section

Materials and Methods: Chemical reagents and solvents were purchased commercially and were used as received without further purification. The ligands L^1, L^2, and L^3 were synthesized according to the literature procedures.[14] The IR spectra were recorded as KBr pellets with a Nicolet Magna-FTIR 560 spectrometer in the 4000–400 cm^{-1} region. Elemental analyses (EA) for C, H, and N were performed with a Perkin–Elmer 240 analyzer. Thermogravimetric analyses were performed with a Shimadzu TGA-50H TG analyzer in the range of 24–700 °C under a nitrogen flow at a heating rate of 5 °C/min for all measurements.

$[Ni(L^1)_{0.5}(3,5\text{-pdc})(H_2O)]\cdot H_2O$ (1): A mixture of $NiCl_2\cdot 6H_2O$ (0.24 g, 1.0 mmol), 3,5-pdc (0.17 g, 1.0 mmol), L^1 (0.24 g, 1.0 mmol), and water (7 mL) was placed in a Teflon®-lined stainless steel vessel and the pH was adjusted to 6–6.5 by addition of dilute NaOH solution (1.0 mol/L). The mixture was sealed and heated at 160 °C for 3 d and then cooled to room temperature at a rate of 5 °C/h. Green crystals were obtained in 58% yield based on Ni. Elemental analysis (%): calcd. C 44.37, H 3.72, N 11.09; found C 42.32, H 3.78, N 11.02. Selected IR data (KBr): $\tilde{\nu}$ = 3470 (s), 3050 (m), 2940 (m), 1605 (s), 1565 (m), 1450 (m), 1403 (m), 1085 (m), 750 (m), 659 (m) cm^{-1}.

$[Co(L^2)(3,5\text{-pdc})]\cdot 2H_2O$ (2): A mixture of $CoCl_2\cdot 6H_2O$ (0.24 g, 1.0 mmol), 3,5-pdc (0.17 g, 1.0 mmol), L^2 (0.19 g, 1.0 mmol), NaOH (0.08 g, 2.0 mmol), and water (7 mL) was placed in a Teflon®-lined stainless steel vessel. The mixture was sealed and heated at 160 °C for 3 d and then cooled to room temperature at a rate of 5 °C/h. Purple crystals were obtained in 56% yield based on Co. Elemental analysis (%): calcd. C 45.34, H 4.70, N 15.55; found C 45.37, H 4.72, N 15.51. Selected IR data (KBr): $\tilde{\nu}$ = 3455 (s), 3056 (m), 2904 (m), 1604 (s), 1566 (m), 1447 (m), 1404 (m), 1091 (m), 817 (m), 655 (m) cm^{-1}.

$[Co(L^3)(3,5\text{-pdc})(H_2O)]\cdot H_2O$ (3): The reaction conditions are similar to those described for **1** except that L^3 was used instead of L^1. Purple crystals were obtained in 52% yield based on Co. Elemental analysis (%): calcd. C 47.70, H 5.27, N 14.64; found C 47.76, H 5.21, N 14.58. Selected IR (KBr): $\tilde{\nu}$ = 3465 (s), 3045 (m), 2952 (m), 1605 (s), 1572 (m), 1440 (m), 1408 (m), 1110 (m), 845 (m), 710 (m), 657 (m) cm^{-1}.

X-ray Crystallography: Suitable single crystals of **1**–**3** were selected and mounted in air onto thin glass fibres. Accurate unit cell parameters were determined by a least-squares fit of the 2θ values, and the intensity data were measured with a Rigaku R-AXIS RAPID IP area diffractometer with Mo-K_α radiation (λ = 0.71073 Å) at room temperature. The intensities were corrected for Lorentz, polarization effects, and for empirical absorption based on the multiscan technique. All the structures were solved by direct methods and refined by full-matrix least-squares fitting on F^2 by SHELX-97. All the non-hydrogen atoms were refined with anisotropic thermal parameters. The aromatic hydrogen atoms were assigned to the calculated positions with isotropic thermal parameters. The crystallographic data for the three compounds are summarized in Table 1.

Table 1. The crystal and structure refinement data for **1**–**3**.

	1	**2**	**3**
Empirical formula	$C_{14}H_{14}N_3NiO_6$	$C_{17}H_{21}CoN_5O_6$	$C_{19}H_{25}CoN_5O_6$
Fw	378.99	450.32	478.37
T [K]	293(2)	293(2)	296(2)
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_1/c$	$Pna2_1$
a [Å]	12.803(3)	9.4191(19)	17.041(3)
b [Å]	9.817(2)	12.478(3)	11.140(2)
c [Å]	12.104(2)	17.794(5)	11.131(2)
β [°]	92.06(3)	115.00(2)	90
Z	4	4	4
D_c [$g\,cm^{-3}$]	1.656	1.578	1.504
V [$Å^3$]	1520.3(5)	1895.4(8)	2113.1(7)
S	1.034	1.038	1.056
R_1, wR_2 (all data)	0.0821, 0.1272	0.0451, 0.0762	0.0443, 0.0917

Supporting Information (see also the footnote on the first page of this article): Table of selected bond lengths and angles for complexes **1**–**3** and Table of hydrogen bonds data for complexes **1**–**3**.

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