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**STRUCTURE AND CHARACTERIZATION OF A 2D COBALT(II) COMPLEX $[\text{Co}(\text{L})_2]_n$
($\text{L} = 3\text{-NITRO-5-(PYRIDINE-4-YL)BENZOATE}$)****D.-Y. Ma, H.-F. Guo, L. Qin**

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The self-assembly of unsymmetrical tecton 3-nitro-5-(pyridin-4-yl)benzoic acid (**HL**) with cobalt chloride under hydrothermal conditions affords a new 2D coordination polymer $[\text{Co}(\text{L})_2]_n$ (**1**, $\text{L} = 3\text{-nitro-5-(pyridin-4-yl)benzoate}$), which is characterized by elemental analysis, infrared spectroscopy, thermogravimetric analysis, powder X-ray diffraction analysis, and single crystal X-ray diffraction. Compound **1** is of the triclinic system, space group *P*-1 with $a = 9.7857(12) \text{ \AA}$, $b = 10.3417(13) \text{ \AA}$, $c = 10.8463(13) \text{ \AA}$, $\alpha = 85.155(2)^\circ$, $\beta = 74.785(2)^\circ$, $\gamma = 88.962(2)^\circ$, $V = 1055.4(2) \text{ \AA}^3$. The crystal structural analysis of complex **1** shows that the cobalt center is six-coordinated in an octahedral geometry by four O atoms from four different **L** ligands and two N atoms from two different **L** ligands; the Co(II) cations are bridged by $\mu_3\text{-L}$ into an interesting two-dimensional network structure. It should be pointed out that the thermal analysis results indicate that complex **1** is quite stable up to 420 °C.

Keywords: cobalt(II) coordination polymer, hydrothermal synthesis, crystal structure, thermal behavior.

INTRODUCTION

The rational design and synthesis of new metal-organic coordination polymers have received increasing attention due to their potential applications in the fields such as catalysis, materials science, biochemistry and so on [1–7]. The rational selection of organic ligands and metals plays an important role in constructing functional coordination polymers, and the weaker non-covalent interactions, such as hydrogen bonds, $\pi\text{--}\pi$ stacking interactions also play key roles in the recognition process forming final 3D architectures [8–10]. Among various inorganic-organic hybrid materials, those of metal N-containing carboxylates constitute a new family [11–15].

As a multidentate ligand, the anion of **L** is an excellent candidate for the construction of supramolecular complexes because it possesses one nitrogen atom of the pyridine ring and two oxygen atoms of the carboxylate group, and can be utilized as a versatile linker for constructing interesting coordination polymers with abundant hydrogen bonds and $\pi\text{--}\pi$ stacking interactions [11, 12].

Based on the above consideration, we report herein the hydrothermal synthesis, crystal structure, and thermal behavior of a new 2D coordination framework **1** based on the unsymmetrical ligand **HL**, namely, $[\text{Co}(\text{L})_2]_n$ (**1**), in which **L** tecton coordinated to cobalt centers acts in the μ_3 fashion. To the best of our knowledge, **1** represents the first example of a metal-based supramolecular framework constructed by 3-nitro-5-(pyridin-4-yl)benzoic acid (**HL**).

Table 1

Selected bond lengths d (Å) and bond angles ω (deg.)

Bond	d	Angle	ω	Angle	ω
Co(1)—O(5) ^{iv}	2.0838(18)	O(5) ^{iv} —Co(1)—O(1)	88.13(7)	O(1)—Co(1)—O(2) ⁱⁱ	90.84(7)
Co(1)—O(2) ⁱⁱ	2.0979(18)	O(1)—Co(1)—O(6) ⁱⁱⁱ	176.43(6)	O(2)—Co(1)—O(6) ⁱⁱⁱ	92.59(7)
Co(1)—N(1) ⁱ	2.169(2)	O(5) ^{iv} —Co(1)—N(1) ⁱ	94.39(8)	O(1)—Co(1)—N(1) ⁱ	87.32(8)
Co(1)—O(1)	2.0927(18)	O(6) ⁱⁱⁱ —Co(1)—N(1) ⁱ	93.86(8)	O(5) ^{iv} —Co(1)—N(3)	85.31(8)
Co(1)—O(6) ⁱⁱⁱ	2.1355(18)	O(6) ⁱⁱⁱ —Co(1)—N(3)	85.90(8)	N(1) ⁱ —Co(1)—N(3)	179.61(6)
Co(1)—N(3)	2.190(2)				

Symmetry codes: ⁱ $-x, -y, 3-z$; ⁱⁱ $-x, -y, 2-z$; ⁱⁱⁱ $1-x, -y, 1-z$; ^{iv} $x, y, 1+z$.

EXPERIMENTAL

Materials and physical measurements. All chemicals purchased were of reagent grade and used without further purification. All syntheses were carried out in 23 ml Teflon-lined autoclaves under autogenous pressure. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240 CHN elemental analyzer. Infrared spectra were recorded (4000—400 cm^{-1}) as KBr disks on a Shimadzu IR-440 spectrometer. Powder XRD investigations were carried out on a Bruker AXS D8-Advanced diffractometer at 40 kV and 40 mA with $\text{CuK}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation. Thermogravimetry analyses (TGA) were performed on an automatic simultaneous thermal analyzer (DTG-60, Shimadzu) under an N_2 flow at a heating rate of 10 $^\circ\text{C}/\text{min}$ between ambient temperature and 800 $^\circ\text{C}$.

Synthesis of 1. A mixture of $\text{CoCl}_2 \cdot 6(\text{H}_2\text{O})$ (0.118 g, 0.5 mmol), HL (0.121 g, 0.5 mmol), NaOH (0.021 g, 0.25 mmol), and H_2O (12 ml) was stirred for 30 min in the air and then sealed in a 23 ml Teflon reactor and kept under autogenous pressure at 160 $^\circ\text{C}$ for 72 h. The mixture was cooled to room temperature at a rate of 5 $^\circ\text{C}/\text{h}$, and red block crystals were obtained in a yield of 42 % based on **L**. Calcd. (%) for $\text{C}_{24}\text{H}_{14}\text{CoN}_4\text{O}_8$: Anal. found (%): C, 52.81; H, 2.57; N, 10.27. Calcd. (%): C, 52.77; H, 2.62; N, 10.28. IR (KBr pellet) (cm^{-1}): 3445(s), 3083(w), 3098(w), 1592(vs), 1576(m), 1529(vs), 1508(w), 1461(m), 1395(s), 1351(vs), 1301(w), 1285(w), 1232(w), 1096(w), 1072(w), 1016(w), 915(w), 877(w), 832(s), 796(m), 779(w), 752(w), 740(m), 719(vs), 683(w), 672(w), 644(m), 544(w), 497(w), 443(w), 410(w).

X-Ray crystallography. A single crystal with the dimensions of 0.29×0.24×0.21 mm was mounted on a glass fiber for data collection which was performed on a Bruker SMART APEXII CCD diffractometer operating at 50 kV and 30 mA with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 296(2) K using a ω scan mode. Data collection and reduction were performed using the APEX II software [16]. Multi-scan absorption corrections were applied using SADABS [16]. The structure was solved by direct methods and refined on F^2 by the full-matrix least squares technique using the SHELX-97 program package [17]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. Selected bond lengths and angles, and H-bonding parameters for complex **1** are given in Tables 1 and 2 respectively.

Crystallographic data. The chemical composition is $\text{C}_{24}\text{H}_{14}\text{CoN}_4\text{O}_8$, formula weight $M_r = 545.32$, triclinic system, $P-1$ space group, $a = 9.7857(12) \text{ \AA}$, $b = 10.3417(13) \text{ \AA}$, $c = 10.8463(13) \text{ \AA}$, $\alpha = 85.155(2)^\circ$, $\beta = 74.785(2)^\circ$, $\gamma = 88.962(2)^\circ$, $V = 1055.4(2) \text{ \AA}^3$, $Z = 2$, $T = 296(2) \text{ K}$, $D_c = 1.716 \text{ g/cm}^3$, $\mu(\text{MoK}\alpha) = 0.878 \text{ mm}^{-1}$, $F(000) = 554$, $S = 1.128$, the final $R = 0.0326$ and $wR = 0.1130$ for 3365 observed reflections with $I > 2\sigma(I)$.

RESULTS AND DISCUSSION

Synthesis and general characterization. The single crystal of complex **1** was obtained by the reaction of cobalt(II) chloride, 3-nitro-5-(pyridin-4-yl)benzoic acid at a 1:1 molar ratio in the water system in a 23 ml Teflon reactor and kept under autogenous pressure at 160 $^\circ\text{C}$ for 72 h. The elemental

Table 2

Hydrogen bonds for compound **1**

D—H \cdots A	$d(\text{D—H}), \text{\AA}$	$d(\text{H}\cdots\text{A}), \text{\AA}$	$d(\text{D}\cdots\text{A}), \text{\AA}$	$\angle(\text{DHA}), \text{deg.}$
C(2)—H(2) \cdots O(7) ^{vi}	0.93	2.59	3.418(2)	149
C(4)—H(4) \cdots O(4) ^v	0.93	2.59	3.505(8)	170
C(16)—H(16) \cdots O(8) ^{vi}	0.93	2.48	3.391(8)	166
C(22)—H(22) \cdots O(6) ⁱⁱⁱ	0.93	2.37	2.940(9)	119

Symmetry codes: ⁱⁱⁱ $1-x, -y, 1-z$; ^v $-1-x, 1-y, 3-z$; ^{vi} $-x, 1-y, 1-z$.

analysis results for complex **1** are highly consistent with the theoretical requirements of their compositions (X-ray analysis results). The title compound is stable in the air and insoluble in water and common organic solvents. In the IR spectra of complex **1**, the features at 1591 cm^{-1} and 1395 cm^{-1} are associated with the asymmetric (COO) and symmetric (COO) stretching vibrations. The $\Delta\nu(\nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-))$ value is 196 cm^{-1} (between 105 cm^{-1} and 200 cm^{-1}), indicating the coordination of **L** with Co(II) in a bridging bidentate mode [18], which is well consistent with the results of the X-ray crystallographic analysis. The features at 1529 cm^{-1} and 1351 cm^{-1} are associated with the asymmetric (NO_2) and symmetric (NO_2) stretching vibrations.

Crystal structure of complex 1. The single crystal X-ray diffraction analysis reveals that compound **1** crystallizes in the $P-1$ space group and has a 2D layered structure. In the asymmetric unit of **1**, there are one Co(II) ion and two **L** ligands. As shown in Fig. 1, the Co(II) ion has an octahedral geometry, which is defined by four oxygen atoms and two nitrogen atoms from six different **L** ligands. The equatorial plane is defined by O1, O2ⁱⁱ, O5^{iv}, and O6ⁱⁱⁱ atoms, while N1 and N1ⁱ occupy the axial position (symmetry codes: ⁱ $-x, -y, 3-z$; ⁱⁱ $-x, -y, 2-z$; ⁱⁱⁱ $1-x, -y, 1-z$; ^{iv} $x, y, 1+z$). The Co—O bond lengths and O—Co—O, O—Co—N angles, all of which are within the range of those observed for other analogical Co(II) complexes [19, 20], range from $2.0838(18) \text{ \AA}$ to $2.190(2) \text{ \AA}$ and $85.31(8)^\circ$ to $179.61(6)^\circ$ respectively.

In the complicated polymeric structure of complex **1**, the **L** ligands exhibit the same distorted Y-shaped $\mu_3\text{-N,O,O}$ bridging mode to link three different cobalt(II) ions. The coordination mode of the

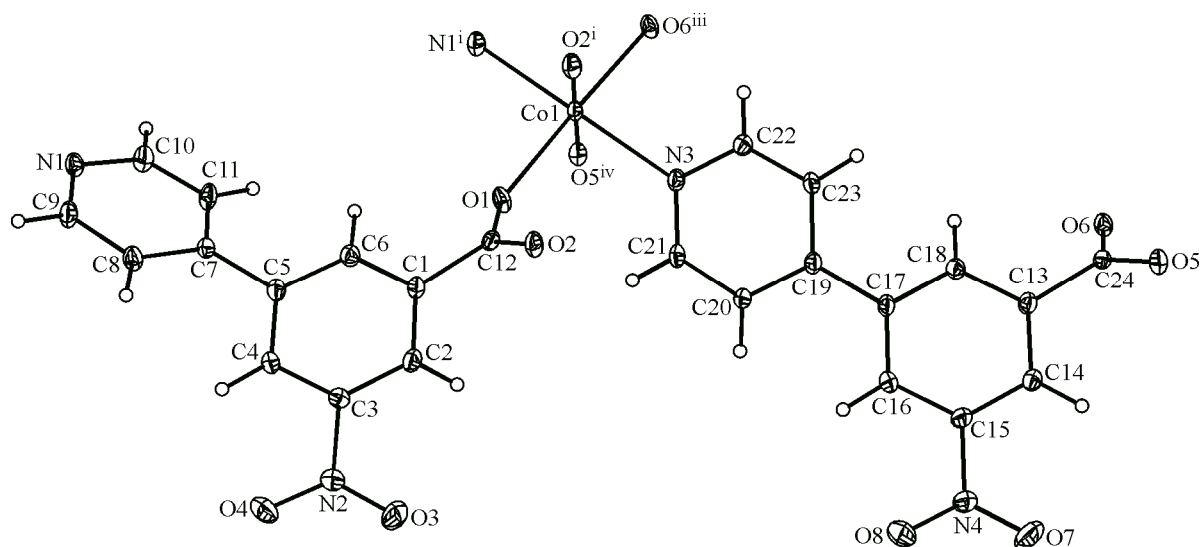


Fig. 1. Thermal ellipsoid plot of the asymmetric unit of **1** (30 % probability ellipsoids).

Symmetry codes: ⁱ $-x, -y, 3-z$; ⁱⁱ $-x, -y, 2-z$; ⁱⁱⁱ $1-x, -y, 1-z$; ^{iv} $x, y, 1+z$

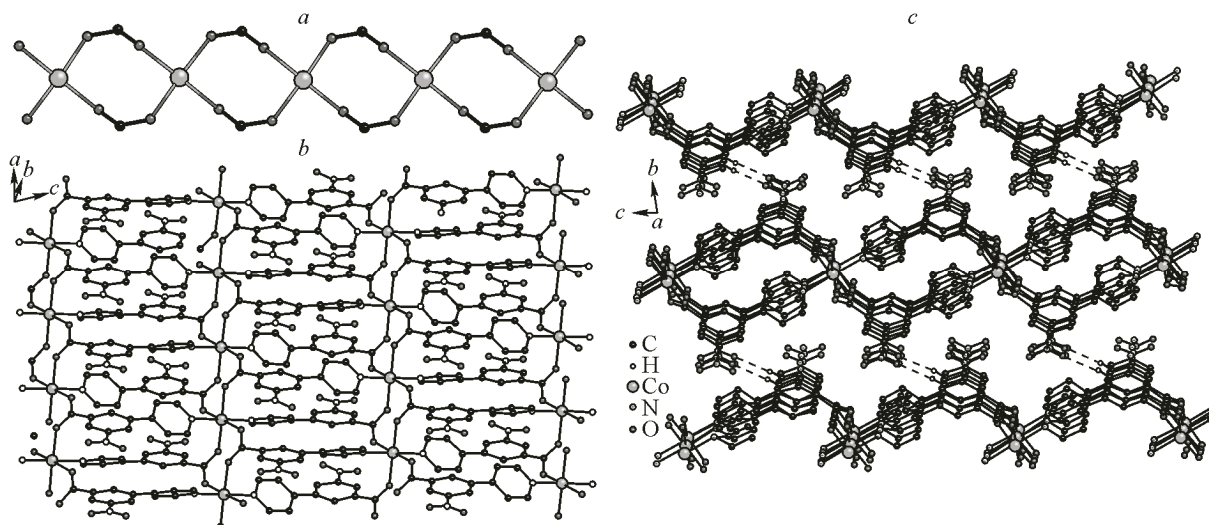


Fig. 2. Co-carboxylate infinite chain of **1** running along the *c* axis (a); view of the 2D layer of **1** (b); view of the 3D framework of **1** formed by hydrogen bonding interactions (dashed lines) (c)

L ligand is similar to that of $[\text{Co}_2(\text{OH})(\text{PBC})_3]_n$ [14], but differs from those of $[\text{Co}(\text{PBC})_2(\text{H}_2\text{O})_4]$ [21] and $[\text{Co}(\text{PBC})_2(\text{H}_2\text{O})]_n$ [15] whose PBC ligands exhibit monodentate—N and μ_2 bridging modes (PBC = 3-pyrid-4-ylbenzoate). The phenyl and pyridyl planes are non-coplanar with a dihedral angle of 32.92° . Based on the connection of μ_3 bridging **L** ligands, cobalt(II) centers were bonded together to form a cobalt-carboxylate chain in the *c* axis direction with the $\text{Co}\cdots\text{Co}$ separations of $4.833(2)$ Å and $4.958(3)$ Å respectively (Fig. 2, a). These chains are further linked into a 2D supramolecular network through the nitrogen atoms of the **L** ligands (Fig. 2, b). Finally, the neighboring layers are self-assembled into an ideal 3D framework through intermolecular $\text{C4}\cdots\text{H4}\cdots\text{O4}^v$ hydrogen bonding interactions (symmetry code: $v - 1 - x, 1 - y, 3 - z$) (Fig. 2, c). Moreover, intramolecular $\text{C}\cdots\text{H}\cdots\text{O}$ hydrogen bonds are also observed. These hydrogen bonds all fall in the normal range; details are available in Table 2.

Powder X-ray diffraction analysis. In order to check the purity of complex **1**, bulk samples were measured by X-ray powder diffraction at room temperature. As shown in Fig. 3, the peak positions of the experimental patterns are in good agreement with the simulated patterns, which clearly indicates the high purity of the complex.

TG analysis. The thermogravimetric analyses (TGA) of compound **1** were performed in the N_2 atmosphere when the sample was heated to 800°C at a constant rate of $10^\circ\text{C}/\text{min}$. The TG curve is depicted in Fig. 4, which shows that compound **1** has good thermal stability since no strictly clear

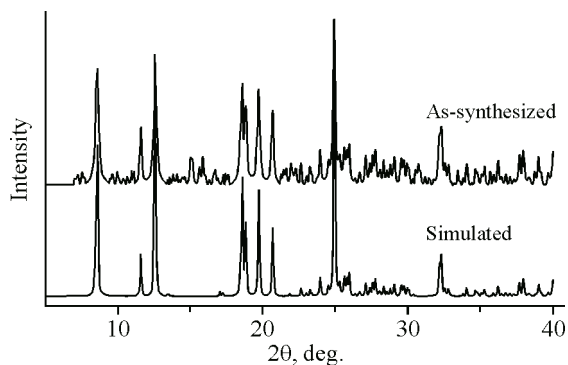


Fig. 3. PXR patterns in complex **1**

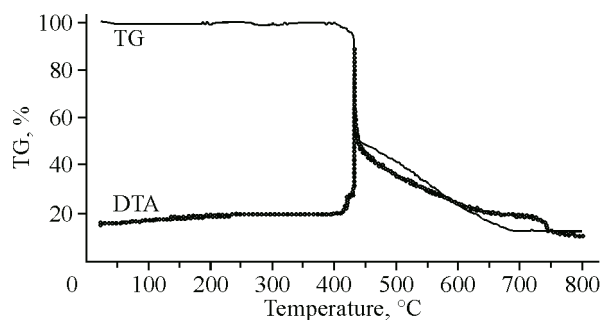


Fig. 4. Thermogravimetric curves (DTA and TG) for compound **1**

weight loss step occurs below 420 °C. The weight loss step occurred above 420 °C, which corresponds to the decomposition of the framework structure. Finally, **1** was completely degraded into CoO with a total loss of 87.53 wt.% (calcd. 86.26 wt.%).

CONCLUSIONS

In conclusion, we have successfully constructed a new 2D coordination polymer $[\text{Co}(\text{L})_2]_n$ based on an unsymmetrical tecton 3-nitro-5-(pyridin-4-yl)benzoate (**L**) ligand under the hydrothermal reaction. This compound shows high thermal stability (up to 420 °C). The successful preparation of the title compound indicates that **L** can be an excellent candidate for the construction of supramolecular complexes, since it has multiple coordination modes. To the best of our knowledge, **1** represents the first example of a metal-based supramolecular framework constructed by the 3-nitro-5-(pyridin-4-yl)benzoic acid (**HL**)

The X-ray diffraction file for **1** in CIF format has been submitted to the Cambridge Crystallographic Data Center as the supplementary publication, CCDC No. 917628. This data can be freely obtained from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or on the web <http://ccdc.cam.ac.uk>.

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