Inorganic Chemistry Communications 50 (2014) 54–57

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

# A novel cadmium-nicotinato linked square-basket metal-organic polymer displaying a thick covalent 2-D layer structure

Jian Cui

*Department of Chemistry, University of Houston-Clear Lake, Houston, TX 77058, United States*

ARTICLE INFO

*Article history:*
Received 10 June 2014
Received in revised form 5 September 2014
Accepted 26 October 2014
Available online 28 October 2014

*Keywords:*
Coordination polymers
Crystal structure
Mixed metal complexes
Cobalt and cadmium
Hydrothermal reactions

ABSTRACT

The reactions of $Cd(NO_3)_2{\cdot}4H_2O$, $Co(NO_3)_2.6H_2O$ with nicotinic acid and 1,2-Di(4-pyridyl) ethylene under hydrothermal reaction conditions resulted in a metal-organic polymer $[(H_2O)Cd(C_6H_4O_2N)_2]_2[(C_6H_4O_2N)_2Co(H_2O)_2]$ **1**. The compound **1** is the first nicotinato-linked mixed cobalt–cadmium compound displaying a square basket-like thick covalent 2-D layer structure.



Introduction: The design and synthesis of the metal-organic polymers via crystal engineering have produced many unique structural features among the coordination polymers reported [1–8]. The crystal engineering of metal-organic network structures rely on the selections of metal centers and organic ligands that may afford desirable covalent bonds, hydrogen bonding linkages, or π–π interactions for the construction of new supramolecular or polymeric complexes. The new network structures utilizing both covalent and hydrogen bonds have attracted much interests recently due to their flexible structural features. By using multidentate building blocks, different network structures may be synthesized. While nicotinato ligand as a multidentate rigid building block has been found to adopt both covalent and hydrogen bonds in many of the reported structures, linkages with mixed metal centers as a building unit may reveal novel interesting structural features for the construction of new metal-organic polymers. It depends upon the coordination requirements of the metal centers in the structures, the linkages in the network, and the possible hydrogen bonds, novel structural features could be obtained. Although many structures containing nicotinato bridges have been reported, the nicotinato structural linkages with mixed cobalt and cadmium metal centers in constructing network structures remain unexplored. Herein we report a novel double cadmium-nicotinato linked square-basket metal-organic polymer displaying a thick covalent 2-D layer structure containing six mixed Cd and Co metal centered rings: $[(H_2O)Cd(C_6H_4O_2N)_2]_2[(C_6H_4O_2N)_2Co(H_2O)_2]$ **1**, the first mixed cobalt and cadmium metal centers bridged via nicotinato ligands.

The reaction of $Cd(NO_3)_2{\cdot}4H_2O$ (0.1543 g,), $Co(NO_3)_2{\cdot}6H_2O$ (0.1455 g) with nicotinic acid (0.2462 g), 1,2-Di(4-pyridyl) ethylene (0.1822 g) and water (3.0 ml) in the mole ratio of 0.5:0.5:2:1:333 at 140 °C under hydrothermal conditions for 3.5 days produced orange crystals of **1**. The orange crystals are suitable for single crystal X-ray diffraction analysis. The details of the crystal structure solutions and refinements are listed in Table 1. The asymmetric unit of structure **1** consists of two unique metal atoms (Fig. 1). The mixed metal centers with cobalt atom displaying octahedral geometry with $\mu^2$-NAs coordination

**Table 1**
Crystal data and structure refinement for $[(H_2O)Cd(C_6H_4O_2N)_2]_2[(C_6H_4O_2N)_2Co(H_2O)_2]$.[a]

| | |
|---|---|
| Formula | $[(H_2O)Cd(C_6H_4O_2N)_2]_2[(C_6H_4O_2N)_2Co(H_2O)_2]$ |
| FW | 1088.41 |
| Space group | $P2_1/n$ |
| *a*/Å | 8.0512(2) |
| *b*/Å | 11.6763(3) |
| *c*/Å | 21.0563(6) |
| *β*/° | 90.8062(11) |
| *V*/Å$^3$ | 1979.27(9) |
| Z | 2 |
| $D_{calc}$/g cm$^{-3}$ | 1.826 |
| μ/mm$^{-1}$ | 12.485 |
| Reflections collected | 13,209 |
| Independent reflections | 3560 [$R_{int}$ = 0.0323] |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Goodness-of-fit on $F^2$ | 1.147 |
| Final R indices [I > 4σ(I)] | R1 = 0.0244, wR2 = 0.0669 |
| R indices (all data) | R1 = 0.0250, wR2 = 0.0682 |

[a] Details of the structure solution, interatomic distances, angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC 1004064).

*E-mail address:* CuiJian@UHCL.edu.

http://dx.doi.org/10.1016/j.inoche.2014.10.025
1387-7003/

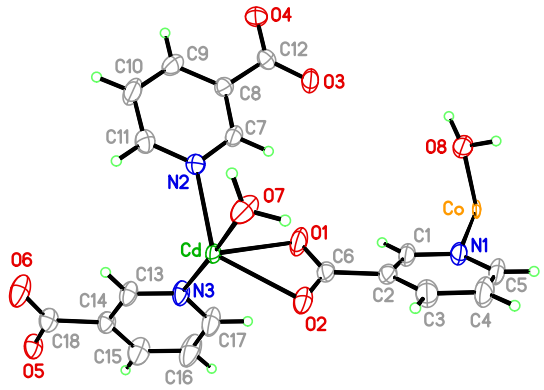


**Fig. 1.** View of the asymmetric unit showing the atom numbering scheme. Thermal ellipsoids are 70% equiprobability envelopes, with hydrogens as spheres of arbitrary diameter.

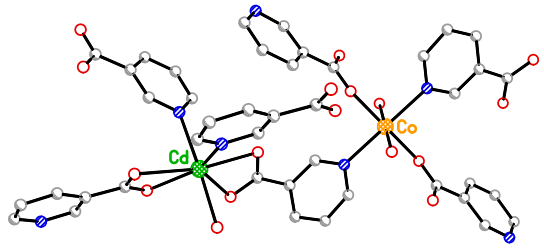


**Fig. 2.** Isotropic view of the complete coordination about Co and Cd in **1**.

through two oxygen and two nitrogen atoms of the nicotinato ligands, and two oxygen atoms (O8, Fig. 1) of the water molecules terminating the covalent chemical bonding at the opposite positions of the octahedral cobalt coordination sphere (Fig. 2). The cadmium atom has seven coordinates with $\mu^2$-NAs coordination through two pairs of oxygen atoms of the carboxylates in the NAs and two nitrogen atoms of the nicotinato ligands, and one water oxygen (O7, Fig. 1) terminating the covalent chemical bonding (Fig. 2). The seven coordination Cd centers linked with octahedral Co metal centers in such a way that each fused four metal centers, Cd…Co…Cd…Co, linked by nicotinato ligands are sharing the octahedral Co metal atoms (Fig. 3) with another fused four metal centered ring.

The propagation of the corner-sharing fused four metal-centered rings in 1 displayed double nicotinato-linked Cd-chains waving through the two-dimensional layer while Co atoms are separated from each other in the linkages (Figs. 4 & 5). The nicotinato-linked Cd-chains in the layers are alternatingly crossing over the Co–NA–Cd linkages (Fig. 5).

The fused four-metal-centered ring are showing square basket-like shape that are linked by two Cd-nicotinato bridged chains on the side when it is viewed down to the b axis (Fig. 6), which ultimately resulted in a novel thick 2-dimensional covalent layer network structure. The Cd-nicotinato bridging chains in the two-dimensional network displayed six metal-centered rings (Fig. 7) that facilitates the complexity of the thick layer.

Due to the nature of the chemical bonding of the nicotinato ligands, strong hydrogen bonds are formed in **1** (Figs. 8 & 9). These hydrogen bonds formed in **1** (O(7)–H(7A)…O(6)#7, 2.737(3); O(7)–H(7B)… O(4)#8, 2.847(3); O(8)–H(8A)…O(6)#3, 2.697(3); O(8)–H(8B)…

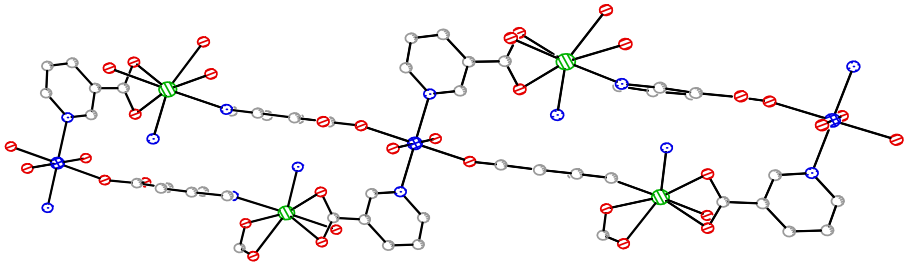

**Fig. 3.** A view down to the c axis about the corner-sharing fused four metal-centered rings in **1**.

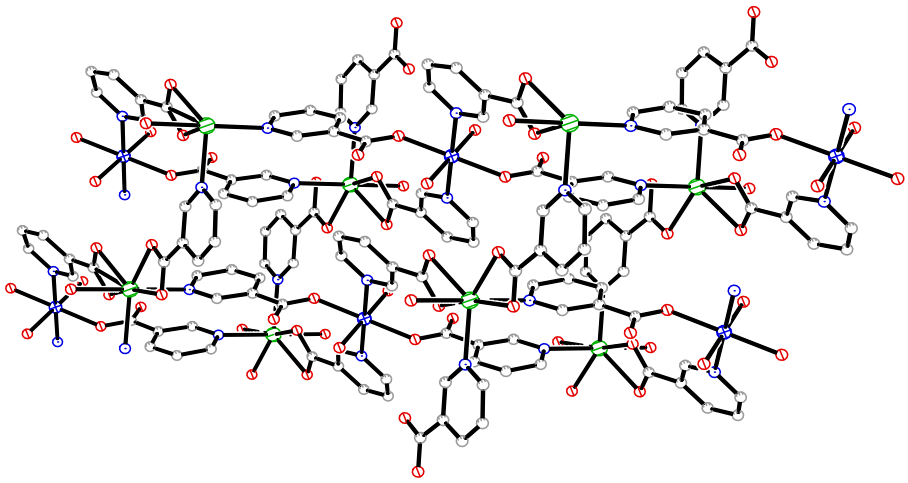

**Fig. 4.** Two dimensional propagation of the corner-sharing fused four metal-centered rings in **1**.