

A Novel Helical Double-Layered Cobalt(II)–Organic Framework with Tetranuclear $[\text{Co}_4(\mu_3\text{-OH})_2]$ Clusters Linked by an Unsymmetrical Pyridylbenzoate Ligand

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A novel cobalt(II)–organic framework, $[\text{Co}_2(\text{OH})(3,4\text{-PBC})_3]_n$ (**1**), has been acquired by the reaction of CoO with an unsymmetrical pyridylbenzoate ligand, 3-pyrid-4-ylbenzoic acid (3,4-PBC). Single-crystal X-ray diffraction studies reveal that it is comprised of $[\text{Co}^{\text{II}}_4(\mu_3\text{-OH})_2]$ clusters linked by the unsymmetrical ligand 3,4-PBC, forming a novel helical double-layered metal–organic architecture. A significant overall antiferromagnetic behavior has been observed for this compound.

The construction of novel metal coordination polymers, based on the interactions between metal ions and organic ligands, has attracted widespread interests because of their potential applications and intriguing variety of architectures and topologies.^{1–6} In particular, the helical coordination polymers are of particular interest, owing to the fundamental role of helicity in biology and their potential utilization in chiral separation, asymmetric catalysis, and nonlinear optic

applications, and many helical metal–organic assemblies and chiral coordination polymers have been constructed on the basis of helical topology.^{7–9}

Lin et al. have explored the synthesis of novel optical and magnetic materials via the use of unsymmetrical pyridyl-carboxylate and analogous bridging ligands.¹⁰ The presence of different functional groups in these kinds of ligands may render interesting properties of the resulting coordination polymers, and the lack of a center of symmetry on these kinds of ligands makes it possible to produce helical polymers. Double-layered structure can be regarded as a unique molecular “floor” directly linked by pillars through covalent bonds, hydrogen bonds, or other weak interactions. The interesting ionic components are concentrated in the central portions of each layer, and the organic portions form hydrophilic layers that sandwich the ionic portions. The double-layered metal–organic frameworks have been reported to show the spongelike dynamic behavior of reducing the interlayer spacing dramatically in response to guest removal, and the charged bilayer compound Na-Adc has been designed as an interesting new biomaterial.¹¹ However, the occurrence of pillared-layer complexes with helical character is particularly rare, although the helical layer motif (a layer

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containing helical chains, usually used in biology) was reported as a new two-dimensional motif.¹² The double helicates, multinuclear double-helical compounds, have recently been attracting considerable interest because it is a prototype for supramolecular self-assembly processes and because of the special feature of the resulting helicates.¹³ In addition, the hetero-double helicate from two different types of strands have been considered as a model for the structural and dynamic features of the double helix of nucleic acids.¹⁴ In this Communication, we report the synthesis, structure, and magnetic properties of a novel helical double-layered metal–organic coordination polymer, $[\text{Co}_2(\text{OH})(3,4\text{-PBC})_3]_n$ (**LAF-1**; Los Alamos Frameworks), which is constructed by tetranuclear $[\text{Co}_4(\mu_3\text{-OH})_2]$ clusters and the unsymmetrical ligand 3,4-PBC.

LAF-1 was synthesized as dark-red crystals by a solvothermal method from CoO (18.7 mg, 0.25 mmol) and 3-pyrid-4-ylbenzoic acid (99.6 mg, 0.5 mmol) in H_2O /dimethylformamide (4/4 mL) in a 23 mL Parr Teflon-lined stainless steel vessel at 105 °C for 72 h.¹⁵ Single-crystal X-ray diffraction reveals that this compound crystallizes in the monoclinic space group $P2_1/c$.¹⁶ Its structure and composition were further confirmed by powder X-ray diffraction (PXRD), elemental analysis, infrared (IR) spectroscopy, and thermogravimetry analysis (TGA).

X-ray crystallographic analysis revealed that, in the asymmetric unit of **LAF-1**, there are two Co^{II} atoms, three 3,4-PBC ligands, and one $\mu_3\text{-OH}$ group (Figure 1). O7 is coordinated to three Co atoms and has a bond valence sum of 0.95 based on the bond lengths of Co–O [1.9950(9), 2.0621(9), and 2.1824(9) Å]. This value suggests that O7 may combine with H, forming a hydroxyl group, which is consistent with the strong OH stretching found in IR. In this structure, two different types of Co atoms can be distinguished, Co1 and Co2. Co1 is coordinated by three carboxylate O atoms [O4, O(5a), and O1], one N atom from four 3,4-PBC ligands, and two $\mu_3\text{-OH}$ groups, forming a distorted CoO_5N octahedron, while Co2 is ligated by three

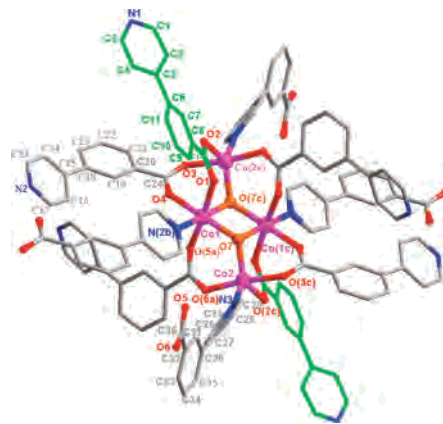


Figure 1. Coordination environments of the Co^{II} ions in **LAF-1**.

3,4-PBC O atoms, one 3,4-PBC N atom, and one $\mu_3\text{-OH}$ group to furnish a distorted CoO_4N trigonal bipyramid. The bond angles between the cis ligands and the Co1 center range from 82.99(4) to 97.77(4)°, whereas the bond angles between the cis ligands and the Co2 center range from 84.43(4) to 127.43(3)°. The Co–O and Co–N distances are all within the normal range found in other reported experiments.¹⁷

LAF-1 contains the rhombus tetranuclear clusters of formula $[\text{Co}_4(\mu_3\text{-OH})_2]$, which can be considered as the secondary building units (SBUs) for construction of the metal–organic architecture of this compound. The two Co sites [Co1 and Co(1c)] along the short diagonal of the rhombus are bridged by two $\mu_3\text{-hydroxides}$, which also bridge the two Co sites along the long diagonal of the rhombus [Co2 and Co(2c)]. All four edges of the rhombic $[\text{Co}_4(\mu_3\text{-OH})_2]$ cluster are also bridged by the $\mu_2(\eta_1, \eta_1)$ carboxylate group of the ligand 3,4-PBC, with the short edge bridged by the double carboxylate groups from two 3,4-PBC, one bridging ligand (3,4-PBC)_{B1}, and one terminal ligand (3,4-PBC)_T, and the long edge bridged by only one carboxylate group from another kind of bridging ligand, (3,4-PBC)_{B2}. The short edge of the rhombus has the shortest $\text{Co}\cdots\text{Co}$ separation [Co1 \cdots Co(2c)] with a distance of 3.1501(5) Å, while Co1 \cdots Co2 in the long edge has a separation of 3.6018(5) Å. Significantly, the 3,4-PBC moieties exhibit a twisted fashion to link each $[\text{Co}_4(\mu_3\text{-OH})_2]$ cluster to another four neighboring $[\text{Co}_4(\mu_3\text{-OH})_2]$ clusters with a dihedral angle of 35.4° between the pyridine ring and the benzene ring of the ligand. As a consequence, a unique helical tubular double layer is built in which the left and right helical chains appear alternatively by sharing the $[\text{Co}_4(\mu_3\text{-OH})_2]$ clusters (Figure 2). Although a number of discrete Co clusters have been reported as single molecular magnets,¹⁸ extended coordinated

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- (15) Synthesis of complex **LAF-1**: A mixture of CoO (18.7 mg, 0.25 mmol) and 3-pyrid-4-ylbenzoic acid (99.6 mg, 0.5 mmol) in H_2O /dimethylformamide (4/4 mL) was stirred at room temperature for 20 min and then transferred and sealed in a 23 mL Parr Teflon-lined stainless steel vessel. This vessel was placed in a stainless steel autoclave, sealed, heated to 105 °C under autogenous pressure for 72 h, and slowly cooled to ambient temperature. Dark-red crystals of **LAF-1** were obtained. Yield: 46 mg. Anal. Calcd for **I**, $\text{C}_{36}\text{H}_{25}\text{Co}_2\text{N}_3\text{O}_7$ (729.45): C, 59.27; H, 3.45; N, 5.76. Found: C, 59.29; H, 3.41; N, 5.79.
- (16) Crystal data for **LAF-1**: $\text{C}_{36}\text{H}_{25}\text{Co}_2\text{N}_3\text{O}_7$, $M_r = 729.45$, dark-red crystals (0.54 × 0.29 × 0.20 mm), monoclinic, space group $P2_1/c$, $a = 11.729(3)$ Å, $b = 13.314(3)$ Å, $c = 19.666(4)$ Å, $\beta = 98.902(3)^\circ$, $V = 3034.2(1)$ Å³, $Z = 4$, $T = 153(2)$ K, $\rho_{\text{calcd}} = 1.597$ Mg·m⁻³, $F(000) = 1488$, $\mu = 1.152$ mm⁻¹, $R1$ ($wR2$) = 0.0265 (0.0697) and $S = 1.053$ for 9301 reflections with $I > 2\sigma(I)$.

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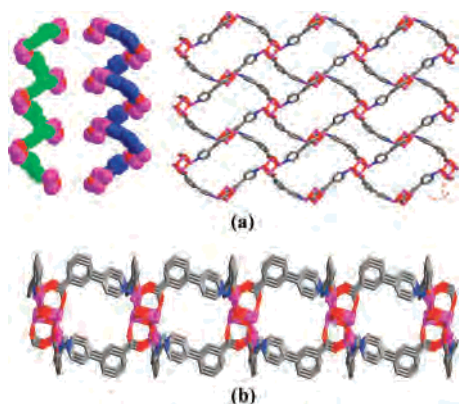


Figure 2. (a) Left: space-filling view of right- and left-handed helical chains. Right: view of a 2D layer constructed via the helical chains. (b) Helical double-layered cobalt(II)-organic architecture.

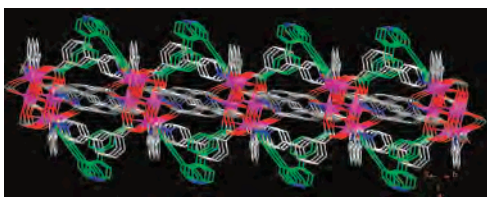


Figure 3. View of the layered structure of **LAF-1**, with the terminal pyridylbenzoate ligands displayed (in green) along both sides of the helical double layer.

networks constructed by such kinds of Co clusters are rare.¹⁹ Moreover, **LAF-1** is the first helical double-layered metal-organic architecture with the unique $[\text{Co}_4(\mu_3\text{-OH})_2]$ clusters as the building units. Within the tubes of this double layer, the double (3,4-PBC)_{B1} units link two neighboring Co₄ clusters into double-stranded chains, and the terminal 3,4-PBC ligands are distributed along both sides of the double layer (Figure 3) and act as pillars between the doubled layers (Figure S2 in the Supporting Information).

We have also studied the bonding behaviors of **LAF-1** using Fourier transform IR spectroscopy (Figure S2 in the Supporting Information). Except a sharp peak at around 3600 cm^{-1} , which is attributed to the $\mu_3\text{-OH}$ group, no broad feature in the range 3000–3800 cm^{-1} was seen, indicative of the absence of water molecules in the title compound. The absence of strong absorption bands around 1720 cm^{-1} confirms the full deprotonation of the carboxylate groups of the ligand 3,4-PBC, as revealed by the single-crystal structure analysis. The peaks at 1570(s) and 1390(s) cm^{-1} correspond to ν_{asym} and ν_{sym} of the chelating carboxylate group, respectively. TGA of **LAF-1** performed under air shows that the framework is stable up to as high as 350 °C, demonstrating the high stability of the robust structure of **LAF-1** with the $[\text{Co}_4(\mu_3\text{-OH})_2]$ clusters as building units. A weight loss of 23.29% occurred in the temperature range 350–500 °C, which corresponds to decomposition of all of the ligands in **LAF-1** and thus formation of Co_2O_3 (calcd 22.74%).

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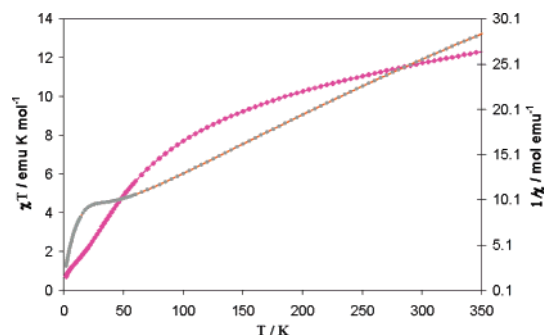


Figure 4. Magnetic susceptibility data for compound **LAF-1**: χT ($\text{emu}\cdot\text{K}\cdot\text{mol}^{-1}$) and $1/\chi$ ($\text{mol}\cdot\text{emu}^{-1}$) vs temperature.

Magnetic susceptibility measurements were performed on microcrystalline samples of **LAF-1** at 0.1 T field in the temperature range 2.0–350 K. As shown in Figure 4, at room temperature the value of product $\chi_m T$ is 11.7 $\text{emu}\cdot\text{K}\cdot\text{mol}^{-1}$, which is slightly larger than the expected value of 10.8 $\text{emu}\cdot\text{K}\cdot\text{mol}^{-1}$ for four noninteracting $S = 3/2$ Co^{II} centers with a g value of 2.4. Upon cooling, the $\chi_m T$ value decreases continuously, reaching a value of 0.712 $\text{emu}\cdot\text{K}\cdot\text{mol}^{-1}$ at 2.0 K. These features indicate a strong antiferromagnetic coupling. A plot of χ_m^{-1} vs T (65–350 K) is essentially linear (Figure 4), and least-squares fitting of the data to the Curie–Weiss law gave $C_m = 6.9683$ $\text{emu}\cdot\text{K}\cdot\text{mol}^{-1}$ and $\theta = -89.54$ K. The Curie constant yields an average g value of 2.4, and the dominating antiferromagnetic interactions are probably responsible for the negative Weiss temperature value even if a contribution from the spin–orbit coupling of Co^{II} is also present.

In conclusion, we have demonstrated the successful construction of a novel cobalt(II)-organic framework with the unsymmetrical pyridylbenzoate ligand. To our knowledge, this compound represents a unique example of coordination polymers that display a helical double-layered structure constructed with a substructure of tetranuclear $[\text{Co}_4(\mu_3\text{-OH})_2]$ clusters. In addition, the overall magnetic behavior of this compound is antiferromagnetic. We are currently extending this work to additional metal ions.

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Supporting Information Available: X-ray crystallographic data in CIF format and complete data for TGA, IR, and PXRD patterns. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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