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Water dimers connect [Cu(*cda*)(py)$_3$] (*cda* = pyridine-4-hydroxy-2, 6-dicarboxylate, py = pyridine) complex units to left- and right-handed helices that form a tubular coordination polymer through supramolecular bonding

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Abstract

The reaction between pyridine-4-hydroxy-2,6-dicarboxylic acid (cdaH$_2$) and Cu(NO$_3$)$_2 \cdot 3$H$_2$O afford products that depend on the reaction conditions applied. In presence of excess of aqueous pyridine (1:2 v/v), equimolar amounts of the reactants form {[Cu(*cda*)(py)$_3$]$_2 \cdot 5$H$_2$O}$_n$ (**1**). In this complex, dimeric water clusters are H-bonded to carboxylate O atoms forming both left- and right-handed helices. These helices are further H-bonded to form a tubular coordination polymer. It crystallizes in the monoclinic space group $P2_1/a$ with $a = 14.235(5)$, $b = 23.097(4)$, $c = 15.542(6)$ Å, $\beta = 114.392(5)°$, $V = 4654(2)$ Å^3, $Z = 4$, $R_1 = 0.0422$, $wR_2 = 0.0992$, $S = 0.899$. When pyridine is used in place of aqueous pyridine, a new coordination polymer, {Cu(*cda*)(py)}$_n$(**2**) is formed that crystallizes in the monoclinic space group $P2_1/c$ with $a = 12.391(5)$, $b = 12.770(5)$, $c = 7.135(5)$ Å, $\beta = 95.155(5)°$, $V = 1124(1)$ Å^3, $Z = 4$, $R_1 = 0.0415$, $wR_2 = 0.0882$, $S = 1.190$. The structure of **2** consists of carboxylate-bridged [Cu(*cda*)(py)] units extending as a zigzag infinite chain where each metal ion shows square-pyramidal geometry. Variable temperature magnetic susceptibility measurements in the temperature range, 2–300 K for **2** is also reported.

Keywords: Supramolecular chemistry; Self-assembly; Helical structure; Coordination polymer; Water dimers

1. Introduction

In the modular approach, coordination tendencies of metal ions toward multi-dentate ligands have been exploited greatly to generate coordination polymers. Success in producing these structures critically depend on understanding and controlling the topological and geometrical relationships between the modules. Compounds that form helical structures in the solid state or in solution, have attracted a lot of interest [1–3] due to their biological relevance. Besides, importance of helicate chemistry is related to the development and understanding of self-assembly processes, influence of noncovalent interactions on supramolecular stereo- or regio-chemistry, and so on. Hence, studies of helical complexes resulting from metal ions and organic ligands have been a major research area of supramolecular chemistry. For a metal–ligand ensemble, propensity for helication depends [4] on the stereoelectronic molecular information encoded in the components (i.e., the ligand and the metal) and the external conditions used for reading this information. A large number of transition metal helicates have been synthesized [5] using multidentate ligands partitioned into a number of discrete metal-binding sites suitable for helication. Purely organic

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compounds forming helical structures through hydrogen-bonding interactions are also known [6]. Herein, we present a neutral complex, $\{[Cu(cda)(py)_3]_2 \cdot 5H_2O\}_n$ where neutral $[Cu(cda)(py)_3]$ units crystallizes in the form of left-as well as right-handed infinite helices through H-bonding with dimeric water clusters. Both these helical chains form an open tubular structure with further H-bonding interactions.

Open tubular frameworks are important [7] as they facilitate understanding the mechanism of the assembly process leading to their formation as well as host–guest chemistry associated with their large uniform internal diameter. Modular synthesis of tubular structures are particularly important as their properties can be made to order through proper designing of the modules. Organic tubular architectures have been built from cyclic peptides [8], calixarene [9], DNAs [10], and other related organic compounds [11]. The discovery of carbon nanotubes [12] has spurt synthesis of metal–ligand hybrid structures in the form of tubes. Several reports of such structures are available [13–16] in the literature.

We show here that either a 1D coordination polymer or a metal–organic tubular open framework structure is formed depending upon the reaction conditions. The complexes are characterized by elemental analysis, X-ray crystallography, vibrational spectroscopy and powder X-ray diffraction.

2. Materials and experimental

2.1. Chemicals and reagents

The metal salts and chelidamic acid ($cdaH_2$) were acquired from Aldrich and used as received.

2.2. Complexes

2.2.1. Synthesis of $\{[Cu(cda)(py)_3]_2 \cdot 5H_2O\}_n$ (1)

A solution containing $Cu(NO_3)_2 \cdot 3H_2O$ (0.24 g; 1 mmol) and chelidamic acid (0.18 g; 1 mmol) dissolved in 25 ml aqueous pyridine (1:1 v/v) on slow evaporation at room temperature, affords light blue crystals of **1** after 14 days in the form of rectangular parallelepiped in 55% yield. *Anal.* Calc. for $C_{44}H_{46}Cu_2N_8O_{15}$: C, 50.15; H, 4.40; N, 10.63. Found: C, 50.22; H, 4.57; N, 10.47%. Main IR features (cm^{-1}, KBr pellet): 3410 br s, 3057 m, 1608 vs, 1454 s, 1390 vs, 1335 m, 1068 vs, 807 s, 751 s, 699 m.

2.2.2. Synthesis of $\{[Cu(cda)(py)]\}_n$ (2)

A solution containing $Cu(NO_3)_2 \cdot 3H_2O$ (0.24 g; 1 mmol) and chelidamic acid (0.18 g; 1 mmol) dissolved in pyridine (10 ml) on slow evaporation at room temperature, affords **2** after 20 h as blue prismatic crystals in 45% yield. *Anal.* Calc. for $C_{12}H_8N_2O_4Cu$: C, 46.83; H, 2.62; N, 9.10. Found: C, 46.92; H, 2.57; N, 9.01%. Main IR features (cm^{-1}, KBr pellet): 1604 s, 1488 m, 1447 s, 1380 vs, 1305 s, 1219 m, 1040 m, 758 m, 691 s.

2.3. Physical measurements

Spectroscopic data were collected as follows: IR (KBr disk, 400–4000 cm^{-1}) Perkin–Elmer Model 1320; X-ray powder pattern (Cu Kα radiation at a scan rate of 3°/min, 293 K) Siefert ISODEBYEFLEX-2002 X-ray generator; thermogravimetric analysis (heating rate of 5 °C/min) Perkin–Elmer Pyris 6. Magnetic measurements were carried out in the Servei de Magnetoquímica at the Universitat de Barcelona on polycrystalline samples with a Quantum Design SQUID MPMS-XL magnetometer. Microanalyses for the compounds were obtained from the Central Drug Research Institute, Lucknow, India.

2.4. X-ray structural studies

Single crystal X-ray data were collected at 100 K on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The linear absorption coefficients, scattering factors for the atoms and the anomalous dispersion corrections were taken from International Tables for X-ray crystallography. The data integration and reduction were processed with SAINT [17] software. An empirical absorption correction was applied to the collected reflections with SADABS [18] using XPREP [19]. The structure was solved by the direct method using SHELXTL [20] and was refined on F^2 by full-matrix least-squares technique using the SHELXL-97 [21] program package. Nonhydrogen atoms were refined aniso-

Table 1
Crystal data and structure refinement for **1** and **2**

	1	**2**
Empirical formula	$C_{44}H_{46}Cu_2N_8O_{15}$	$C_{12}H_8CuN_2O_5$
Formula weight	1053.97	323.74
Temperature (K)	100	100
Radiation	Mo Kα	Mo Kα
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/a$	$P2_1/c$
a (Å)	14.235(5)	12.391(5)
b (Å)	23.097(5)	12.770(5)
c (Å)	15.542(5)	7.135(5)
α (°)	90.00	90.00
β (°)	114.392(5)	95.155(5)
γ (°)	90.00	90.00
V (Å^3)	4654(2)	1124.4(1)
Z	4	4
ρ_{calc} (Mg/m^3)	1.504	1.912
μ (mm^{-1})	0.992	1.965
$F(000)$	2176	652
Reflections collected	31 015	7186
Independent reflections	9598	2341
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Good-of-fit	0.899	1.190
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0422$ $wR_2 = 0.0992$	$R_1 = 0.0415$ $wR_2 = 0.0882$
R indices (all data)	$R_1 = 0.0526$ $wR_2 = 0.1053$	$R_1 = 0.0573$ $wR_2 = 0.1340$