Journal of Solid State Chemistry 211 (2014) 25–31

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

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

Three new homochiral coordination polymers involving two three-dimensional structural architectures: Syntheses, structures and magnetic properties

Tzu-Ling Chao, Chen-I. Yang*

Department of Chemistry, Tunghai University, Taichung 407, Taiwan

ARTICLE INFO

Article history:
Received 23 September 2013
Received in revised form
25 November 2013
Accepted 1 December 2013
Available online 12 December 2013

Keywords:
Homochiral
Coordination polymer
Magnetic properties
Antiferromagnetic

ABSTRACT

The preparations and properties of three new homochiral three-dimensional (3D) coordination polymers, $[M(D\text{-cam})(pyz)(H_2O)_2]_n$ (M=Co (**1**) and Ni (**2**); *D*-H_2cam=(+) *D*-camphoric acid; pyz=pyrazine) and $[Mn_2(D\text{-cam})_2(H_2O)_2]$ (**3**), under solvothermal conditions is described. Single-crystal X-ray diffraction analyses revealed that all of compounds are homochiral 3D structure. **1** and **2** are isostructural and crystallize in the trigonal space group $P3_221$, while **3** crystallizes in monoclinic space group $P2_1$. The structure of **1** and **2** consists of metal-*D*-cam helical chains which are pillared with pyrazine ligands into a 3D framework structure and **3** features a 3D homochiral framework involving one-dimensional manganese-carboxylate chains that are aligned parallel to the *b* axis. Magnetic susceptibility data of all compounds were collected. The findings indicate that μ_2-pyrazine dominate weak antiferromagnetic coupling within **1** and **2**, while **3** exhibits antiferromagnetic behavior through the carboxylate groups of *D*-cam ligand.

1. Introduction

During the past decades in the field of crystal engineering, much effort has been devoted to the design and synthesis of new homochiral coordination frameworks from the combination of metal ions and multifunctional bridging ligands, owing to their potential applications in the field of chemical and pharmaceutical industries ranging from enantioselective separation, catalysis, sensors, and non-linear optics [1–11]. In the category of magneto-chiral dichroism (MChD) studies, the chirality of the synthesized compounds must be maintained at the molecular as well as the macroscopic levels, and the key structural or electronic characteristics that govern the resulting magnetic ground states and their relationship to modulated bulk magnetic properties needs to be determined [12–18]. The development of more chiral magnetic materials would open opportunities for gaining a better understanding of the fundamental aspects that influence crystal nucleation and growth and hence contribute to the development of multi-functional materials.

One of the important features of polycarboxylate bridging ligands with metal ions is that they can serve as precursors of a wide variety of polynuclear cluster-based metal complexes, ranging from discrete entities to multidimensional systems. The (+) *D*-camphoric acid (*D*-H_2cam) organic ligand, it consists of a rigid banding backbone based on a cyclopentane ring and two freely rotating carboxylate groups. Such a configuration may offer a variety of coordination modes for the carboxylate groups depending on the reaction conditions required to fit the coordination preference of the metal centers. Meanwhile, the two carboxylates of *D*-H_2cam may allow a significant magnetic exchange pathway between the bridged paramagnetic centers with diverse magnetic behaviors, such as ferromagnetism and magnetic ordering, since they not only connect the metal ions to multidimensional structures but also shorten the distance between metal ions, which would be expected to contribute to a significant magnetic exchange pathway [19–30]. Meanwhile, the use of a simple pyrazine (pyz) as a bridging ligand is very effective to investigate the magnetic exchange pathway [31–34]. Few papers are reported in which pyz-bridged copper(II) complexes show ferromagnetic coupling [35,36]. Along with these concepts, the combinations of *D*-H_2cam and pyz ligands represent good candidates for the construction of new homochiral coordination polymer with interesting magnetic properties.

Herein we report on the solvothermal synthesis and structural characterization of three new homochiral coordination polymers, $[M(D\text{-cam})(pyz)(H_2O)_2]_n$ (M=Co (**1**) and Ni (**2**); *D*-H_2cam=(+) *D*-camphoric acid; pyz=pyrazine) and $[Mn_2(D\text{-cam})_2(H_2O)_2]$ (**3**). Compounds **1** and **2** show a 3D framework consisting of metal-*D*-cam helical chains which pillared with pyrazine, while compound **3** adopt a three-dimensional homochiral framework

---

* Corresponding author. Tel.: +886 4 23590248x313; fax: +886 4 23590426.
E-mail address: ciyang@thu.edu.tw (C.-I. Yang).

0022-4596/$ - see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jssc.2013.12.001

involving one-dimensional manganese-carboxylate chains. The magnetic analysis reveal that antiferromagnetic interactions were mediated in compounds **1** and **2** through pyrazine ligand and in compound **3** through carboxylate of *D*-cam ligand. Thermogravimetric analyses (TGA), and powder X-ray diffraction (PXRD) of these three new homochiral frameworks were also studied.

2. Experimental

2.1. Synthesis

All reagents and solvents were commercially available and were used as supplied without further purification.

2.1.1. $[M(D\text{-cam})(pyz)(H_2O)_2]_n$ (M=Co (**1**) and Ni (**2**))

Compounds **1** and **2** were obtained in a typical procedure, a mixture of $M(OAc)_2 \cdot 4H_2O$ (0.10 mmol) (M=Co and Ni), *D*-H_2cam (0.05 mmol), pyrazine (0.5 mmol) and DMF/H_2O (3/3 mL) was heated at 80 °C for two days. After the mixture was gradually cooled to room temperature, single crystals of compounds suitable for X-ray study were obtained. The solid product was washed with water and isolated by suction filtration. A powder X-ray diffraction pattern of the bulk sample compared well with the pattern simulated from the single-crystal data (vide infra).

$[Co(D\text{-cam})(pyz)(H_2O)_2]_n$ (**1**): The yield was 66% based on *D*-H_2cam. Anal. Calcd for $C_{14}H_{20}CoN_2O_6$ (M_r=370.24): C, 45.29; H, 5.43; N, 7.50. Found: C, 45.79; H, 5.40; N, 7.35. IR data (KBr disk, cm^{-1}): 3334 (br, vs), 2974 (vs), 2932 (s), 1532 (vs, C=O), 1455 (s), 1428 (vs), 1417 (vs), 1378 (vs), 1361 (vs), 1323 (m), 1288 (s), 1170 (s), 1135 (w), 1084 (s), 1059 (s), 1006 (w), 989 (w), 857 (w), 830 (w), 804 (s), 775 (s), 711 (s), 599 (m), 471 (s).

$[Ni(D\text{-cam})(pyz)(H_2O)_2]_n$ (**2**): The yield was 49% based on *D*-H_2cam. Anal. Calcd for $C_{14}H_{20}NiN_2O_6$ (M_r=369.05): C, 45.52; H, 5.18; N, 7.58. Found: C, 44.99; H, 5.47; N, 7.18. IR data (KBr disk, cm^{-1}): 3344 (br, vs), 2974 (vs), 2931 (s), 1531 (vs, C=O), 1455 (m), 1428 (vs), 1395 (vs), 1362 (vs), 1322 (m), 1287 (s), 1240 (s), 1170 (s), 1135 (w), 1086 (s), 1063 (s), 1009 (w), 981 (w), 872 (w), 831 (w), 808 (s), 781 (s), 714 (s), 596 (m), 481 (s).

2.1.2. $[Mn_2(D\text{-cam})_2(H_2O)_2]_n$ (**3**)

A mixture of $Mn(OAc)_2 \cdot 4H_2O$ (0.10 mmol), *D*-H_2cam (0.05 mmol), pyrazine (0.5 mmol) and MeCN/H_2O (3/3 mL) was heated at 80 °C for two days. After the mixture was gradually cooled to room temperature, single crystals of compounds suitable for X-ray study were obtained. The solid product was washed with water and isolated by suction filtration. A powder X-ray diffraction pattern of the bulk sample compared well with the pattern simulated from the single-crystal data (vide infra). $[Mn_2(D\text{-cam})_2(H_2O)_2]_n$ (**3**): The yield was 44% based on *D*-H_2cam. Anal. Calcd for $C_{20}H_{32}Mn_2O_{10}$ (M_r=542.34): C, 44.27; H, 5.95. Found: C, 44.58; H, 5.73. IR data (KBr disk, cm^{-1}): 3298 (br, vs), 2969 (vs), 2880 (m), 1563 (vs, C=O), 1460 (s), 1410 (vs), 1371 (s), 1291 (m), 1177 (w), 1128 (w), 1084 (s), 1002 (w), 930 (w), 808 (m), 796 (m), 756 (m), 694 (w), 607 (w), 507 (m), 470 (w).

2.2. X-ray crystallography

The X-ray intensity data for the four compounds were collected on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized Mo*K*α radiation (λ=0.71073 Å). The crystal structure was solved by means of direct methods and refined employing full-matrix least squares on F^2 (SHELXTL-97) [37]. The hydrogen atoms attached to carbons were generated geometrically. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. For compounds 1 and 2, the C6 in *D*-cam ligand showed disordered with its symmetrical equivalent position with the occupancies of 0.5. The refinements converged with crystallographic agreement factors are summarized in Table 1 and selected interatomic distances are listed in Table 2.

Table 1
Crystallographic data for **1**–**3**.

	1	**2**	**3**
Formula	$C_{14}H_{20}CoN_2O_6$	$C_{14}H_{20}N_2NiO_6$	$C_{20}H_{32}Mn_2O_{10}$
f_w	371.25	371.01	542.34
Crystal system	Trigonal	Trigonal	Monoclinic
Space group	$P3_221$	$P3_221$	$P2_1$
a/Å	7.0182 (11)	6.9146(6)	10.6700(15)
b/Å	7.0182(11)	6.9146(6)	7.4055(11)
c/Å	28.121(9)	28.228(5)	14.410(2)
α/°	90	90	90
β/°	90	90	90.240(3)
γ/°	120	120	90
V/Å^3	1199.5(5)	1168.8(2)	1138.6(3)
Z	3	3	2
T/K	150(2)	150(2)	150(2)
D_c/g cm^{-3}	1.542	1.581	1.582
μ/mm^{-1}	1.105	1.278	1.162
$(\Delta\rho)$max, min/e Å^{-3}	1.732, −1.153	2.460, −2.435	1.569, −0.987
Measured/independent (Rint) reflections	8313/1781 (0.0925)	8321/1773 (0.0462)	8386/4734 (0.0368)
Observed reflections [$I > 2\sigma(I)$]	1527	1667	3733
Goodness-of-fits on F^2	1.081	1.038	1.059
R_1[a], wR_2[b] (all data)	0.0820, 0.1941	0.0756, 0.1927	0.0891, 0.1961
R_1[a], wR_2[b] ($I > 2\sigma$ (I))	0.0712, 0.1862	0.0731, 0.1906	0.0722, 0.1847

[a] $R_1 = (\Sigma||F_O| - |F_C||)/\Sigma|F_O|$.
[b] $wR_2 = [\Sigma[w(F_O{}^2 - F_C{}^2)^2]/\Sigma[w(F_O{}^2)^2]]^{1/2}$.

Table 2
Selected bond distances (Å) for compounds **1**–**3**.

1			
O(12)–Co(1)	2.121(4)	Co(1)–N(2)	2.117(6)
O(13)–Co(1)	2.072(4)	Co(1)–O(12)#2	2.121(4)
Co(1)–O(13)#2	2.072(4)	Co(1)–N(1)	2.157(7)
2			
Ni(1)–O(2)	2.063(4)	Ni(1)–O(1)#2	2.083(4)
Ni(1)–O(2)#2	2.063(4)	Ni(1)–O(1)	2.083(4)
Ni(1)–N(2)	2.079(7)	Ni(1)–N(1)	2.086(6)
3			
Mn(1)–O(5)	2.079(5)	Mn(2)–O(9)	2.075(5)
Mn(1)–O(12)	2.106(5)	Mn(2)–O(11)	2.130(5)
Mn(1)–O(4)#1	2.123(5)	Mn(2)–O(2)#2	2.159(4)
Mn(1)–O(10)	2.172(5)	Mn(2)–O(1)	2.211(4)
Mn(1)–O(3)	2.182(5)	Mn(2)–O(8)	2.213(5)
Mn(1)–O(4)	2.565(5)	Mn(2)–O(2)	2.453(4)

2.3. Physical measurements

Variable temperature dc magnetic susceptibility measurements were collected on microcrystalline samples, restrained in eicosane to prevent torquing, on a Quantum Design MPMS-XL7 magnetometer equipped with a 7.0 T magnet operating in the range of 2.0–300.0 K. Diamagnetic corrections were estimated from Pascal's constants [38] and subtracted from the experimental susceptibility data to obtain the molar paramagnetic susceptibility of the compounds. Elemental analyses were performed using an Elemental vario EL III analyzer. Thermogravimetric analysis was performed on a Seiko Instrumental, Inc., EXSTAR 6200 TG/DTA analyzer with a heating rate of 5 °C/min under a nitrogen