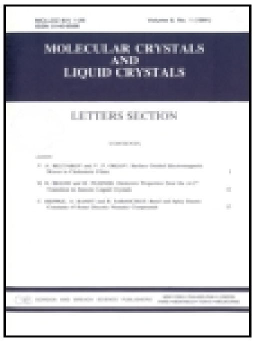

Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

1D infinite helical water chain encapsulated in a supramolecular complex based on amino acid derivate

Fan Yu & Bao Li

To cite this article: Fan Yu & Bao Li (2016) 1D infinite helical water chain encapsulated in a supramolecular complex based on amino acid derivate, Molecular Crystals and Liquid Crystals, 625:1, 253-258, DOI: 10.1080/15421406.2015.1073568

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1073568

MOL. CRYST. LIQ. CRYST.
2016, VOL. 625, 253–258
http://dx.doi.org/10.1080/15421406.2015.1073568

1D infinite helical water chain encapsulated in a supramolecular complex based on amino acid derivate

Fan Yu[a] and Bao Li[b]

[a]Key Laboratory of Optoelectronic Chemical Materials and Devices of Ministry of Education, School of Chemistry and Environmental Engineering, Jianghan University, Wuhan, Hubei, P. R. China; [b]Department of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan, Hubei, P. R. China

ABSTRACT
An oligonuclear complex based on amino acid derivate had been synthesized and structurally characterized, which exhibits a three-dimensional (3D) supramolecular framework constructed from the mono-cobalt units and helical water chains stabilized in this complex. Additionally, the compound was characterized by thermogravimetric analysis (TGA), IR spectroscopy, and elemental analysis.

KEYWORDS
Amino acid derivate; cobalt; helical; water chain

1. Introduction

Systematic investigation of water aggregates formed by variable nuclearities has attracted great interest due to their potential applications, biological, and chemical processes [1–3]. The best understanding of hydrogen bonding interactions and rearrangement dynamics of discrete water clusters, infinite water chains, and sheets would be for achieving an accurate description of liquid water and its anomalous properties [1–5]. With this consideration in mind, several types of interesting water aggregates, such as water clusters $(H_2O)_n$ [4–6], one-dimensional (1D) water chains [7–9], two-dimensional (2D) water layers [10–12], and even three-dimensional (3D) water structures [13,14], have been synthesized and documented in recent decades. Comparably, the infinite water chains attract much more attention due to the vital role of controlling proton fluxes in a large number of biomolecules, facilitating the selective permeation of water across membranes, and stabilizing the native conformation of biopolymers [15–17]. In addition, much interest has been also focused on the construction of helical water chains because they are very essential to understand hydrogen bonds and other noncovalent interactions in many important biopolymers [18,19].

Despite some success has been achieved on water chains or helical water chains, it is still extremely difficult to construct thus water aggregates artificially because of the poor understanding of structural constraints required in stabilizing helical chains [20,21]. Therefore, the modulation and stabilization of thus water chains is a long-standing challenge. The structures and types of water aggregates have good relationships with the synthetic achiral or chiral building block or supramolecular networks, which have

CONTACT Fan Yu ✉ yufan0714@163.com Key Laboratory of Optoelectronic Chemical Materials and Devices of Ministry of Education, School of Chemistry and Environmental Engineering, Jianghan University, Wuhan, Hubei 430056, P. R. China; Bao Li ✉ libao@hust.edu.cn Department of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, P. R. China.

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

provided accurate and detailed information about hydrogen bonding in diverse water clusters trapped in these host matrices [22]. With this consideration in mind, we set out to select amino acid derivates as the building components to construct chiral scaffolds to trap helical water aggregates [23]. Herein, we present a new discrete mononuclear compound derived from amino acid derivate, $[Co(L)(H_2O)_4]\cdot5H_2O$ (**1**) (L = 4-((1-carboxy-2-(4-hydroxyphenyl)ethylamino)methyl)benzoic acid), which interestingly stabilizes infinite helical 1D water chains in the host of supramolecular structure.

2. Experimental section

2.1. *General*

All of the chemicals were obtained from commercial sources and used without further purification. The synthesis of the ligand was referred by Wang et al. [23].

2.2. *Synthesis and crystallization*

A solution of $Co(NO_3)_2\cdot3H_2O$ (0.030g) in 5mL water was mixed with ligand (H_2L) (0.010g) in 10mLH_2O with addition of several drops of 0.2molL^{-1} NaOH solution. The mixture was sealed in a Pyrex tube and heated to 50 °C for half day, and then standed at room temperature. The red block-shaped crystals obtained were filtered and washed with water. Yield of the reaction was ca. 30% based on the ligand. Anal. Calcd. for $C_{17}H_{33}NO_{14}Co$: H 6.22%, C 38.21%, N 2.62%; found H 5.47%, C 37.85%, N 2.89%. IR: 3440, 1606, 1529, 1387, 1173, 1095, 1020, 861, 784, 760.

2.3. *X-ray structure determination*

X-ray diffraction data of **1** (0.20 mm × 0.2 mm × 0.1 mm) were collected on Oxford Gemini S Ultra at 293 K. Crystal structure were solved by the direct methods implemented in the SIR 97 program package and refined using the full-matrix least-square method on F^2 with the SHELXL-97 package [24]. The data reduction was carried out by the program CrysAlis RED. All non-hydrogen atoms were refined anisotropically. All H atoms were placed geometrically, with C–H = 0.93 (aromatic) or 0.96 Å (CH_2), and refined using a riding-atom model, with $U_{iso}(H) = 1.2U_{eq}(C)$. The hydrogen atoms attached to oxygen of water were refined with O–H = 0.85Å, and $U_{iso}(H) = 1.2U_{eq}(O)$, and fixed at the ideal positions with the consideration of the proper positions of water molecules. O7 was refined isotropically. Crystal data, data collection, and structure refinement details are summarized in Table 1. Future details for structural analysis were summarized in Table 1. CCDC-1005144 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/datarequest/cif.

3. Results and discussion

3.1. *X-ray structure determination*

The complex **1** was synthesized by slow evaporation at room temperature. The compositions of **1** were further deduced from X-ray single crystal diffraction, elemental analyses, and IR spectrum.

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

Compound reference	1
Chemical formula	$C_{17}H_{33}CoNO_{14}$
Formula mass	534.37
Crystal system	Orthorhombic
a (Å)	7.9047(3)
b (Å)	11.6284(6)
c (Å)	26.0115(13)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
Unit cell volume (Å^3)	2390.95(19)
Temperature (K)	293(2)
Space group	*P*2(1)2(1)2(1)
No. of formula units per unit cell, *Z*	4
No. of reflections measured	7911
No. of independent reflections	4126
R_{int}	0.0271
Final R_1 values ($I > 2\sigma(I)$)	0.0321
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0830
Final R_1 values (all data)	0.0370
Final $wR(F^2)$ values (all data)	0.0849

Crystal data are listed in Table 1. Compound 1 crystallizes in the orthorhombic space group *P*2(1)2(1)2(1). The asymmetric unit of **1** contains a complete mono-nuclear cobalt unit, and five lattice water molecules, shown in Fig. 1. The central cobalt ion adapts octahedral configuration and is coordinated by one pyridyl-N atom, one carboxylate oxygen atom, and four coordinated water molecules, where the basal plane is formed by one pyridyl-N atom and three coordinated water molecules, and the axial positions are occupied by two oxygen atoms from water molecule and carboxylate group. Each central cobalt ion was chelated by the fully de-protonated amino acid derivate. The Co–N and –O bond distances range from 2.036(6) to 2.167(8) Å, in accordance with the Co(II) state. In addition, the L ligand was folded caused by the strong π–π interaction (3.749 Å) between two aromatic rings (centroid-to-centroid). The supramolecular network of **1** is shown in Fig. 2, indicating that hydrogen bonding interaction between the carboxylate groups and coordinated aqua molecules plays a pivotal role in assembling the discrete mono-nuclear entities toward higher dimensionality. As a result, the 3D supramolecular network with regular 1D helical channels along the *a*-axis is generated by thus successive interactions.

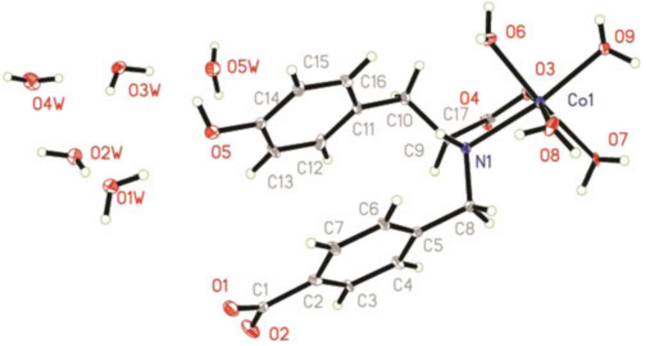

Figure 1. The molecular structure of (**1**), showing the atom-labeling scheme and displacement ellipsoids drawn at the 30% probability level.

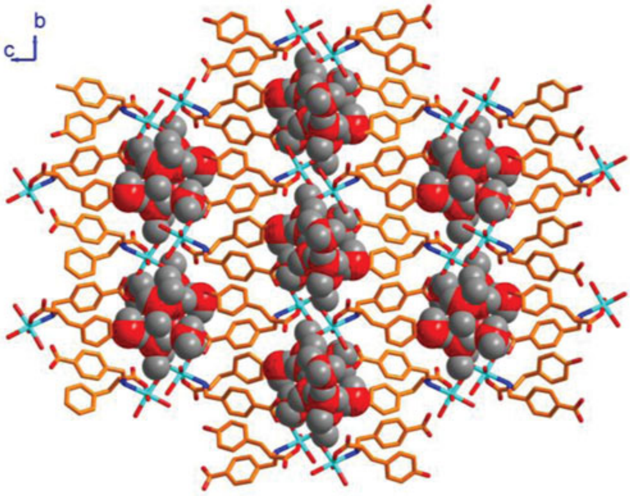

Figure 2. The perspective of 3D crystal packing model along the crystallographic *a*-axis direction.

Each channel accommodates a one-dimensional helical water chain, as shown in Fig. 3. In this helical chain, two of lattice waters (O1W and O2W) associated with themselves together by hydrogen bonds give rise to R-helical assembly. The other water molecules (O3W, O4W, and O5W) are ligated together via hydrogen bonding interactions, and bind onto the helical water chain. Each water molecule in the chain forms two hydrogen bonds, one as a donor and the other as an acceptor, and all of the hydrogen bonding distances range from 2.725(10) to 2.899(15)Å (O···O distances). All of the 1D helical water chains are anchored onto the supramolecular host by versatile hydrogen bonding interactions of O-H·$O_{\text{coordinated water}}$ with the distances from 2.647(12) to 2.867(11)Å (O···O distances). Here, both host–host, water–host, and water–water interactions are important for the stability of the overall structure.

3.2. *IR analysis*

The solid Fourier transform infrared spectroscopy (FTIR) spectra of complex **1** shows a very intense broad band around 3400 cm^{-1} attributed to the water molecules [25]. In the IR spectra of compound, the broad peaks near ca. 3400 cm^{-1} indicate the presence of water molecules. The IR spectra also show characteristic absorption bands mainly attributed to the asymmetric (ν_{as}: ca. 1600 cm^{-1}) and symmetric (ν_s: ca. 1385 cm^{-1}) stretching vibrations of the carboxylate groups. No band in the region 1690–1730 cm^{-1} indicates complete deprotonation of the carboxylate groups, and is consistent with the result of the X-ray diffraction analysis [26].

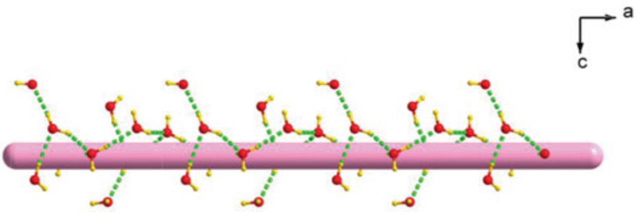

Figure 3. The perspective view of the helical water chain in the lattice of supramolecular structure.

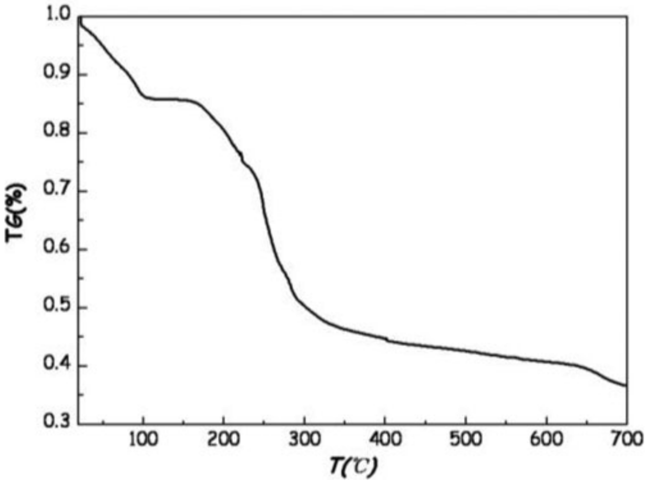

Figure 4. TG curve of **1**.

3.3. *TGA analysis*

We have also studied the thermal stability of the water cluster by thermogravimetric analysis (TGA), shown in Fig. 4. TGA studies showed total water loses occur in two stages, and an 16% weight loss was observed between 25 °C and 120 °C, which is almost equivalent to a loss of five water molecules.

4. Conclusions

In summary, a self-assembled, 1D helical chains trapped within a supramolecular host has been characterized by X-ray crystallography, TGA, and IR spectra. We succeed in modulating not only the structural motifs of the metal–organic framework, but also the helical 1D water aggregates by employment of new host constructed from the amino acid derivate. Thus, result illustrates the sensitive dependence of water aggregates upon the details of their environment. This unique water aggregate may be important in providing insight into the hydrogen bonding motifs between host and waters in bio-systems.

Funding

The authors gratefully acknowledge the National Natural Science Foundation of China (nos. 51403079, 21101066) and Wuhan Science and Technology Bureau (grant no. 201271031382) for generous financial support.

References

[1] Ludwig, R. (2001). *Angew. Chem. Int. Ed.*, *40*, 1808.
[2] Ball, P. (1999). *H2O: A Biography of Water*, Weidenfeld & Nicolson: London.
[3] Liu, K., Cruzan, J. D., & Saykally, R. J. (1996). *Science*, *271*, 929.
[4] Bi, Y., Liao, W., Zhang, H., & Li, D. (2009). *Cryst. Eng. Comm.*, *11*, 1213.
[5] Pan, Q. H., et al. (2008). *Angew. Chem., Int. Ed.*, *47*, 7868.
[6] Sun, D., Wang, D. F., Zhang, N., Huang, R. B., & Zheng, L. S. (2010). *Cryst. Growth Des.*, *10*, 5031.
[7] Dai, F. N., He, H. Y., & Sun, D. F. (2008). *J. Am. Chem. Soc.*, *130*, 14064.
[8] Mukherjee, A., Saha, M. K., Nethaji, M., & Chakravarty, A. R. (2004). *Chem. Commun.*, 716.

[9] Fei, Z., et al. (2005). *Angew. Chem. Int. Ed.*, *44*, 5720.
[10] Sun, D., et al. (2010). *Cryst. Growth Des.*, *10*, 4642.
[11] Hao, H., Sun, D., Liu, F., Huang, R., & Zheng, L. (2011). *Cryst. Growth Des.*, *11*, 5475.
[12] Janiak, C., Scharamann, T. G., & Mason, S. A. (2002). *J. Am. Chem. Soc.*, *124*, 14010.
[13] Carballo, R., Covelo, B., Lodeiro, C., & Vázquez-López, E. M. (2005). *Cryst. Eng. Comm.*, *7*, 294.
[14] Yu, F., & Li, B. (2011). *Inorg. Chim. Acta*, *376*, 218.
[15] Sahoo, S., Kundu, T., & Banerjee, R. (2011). *J. Am. Chem. Soc.*, *133*, 17950.
[16] Luo, G., et al. (2012). *Inorg. Chem. Comm.*, *20*, 290.
[17] Tajkhorshid, K., et al. (2002). *Science*, *296*, 525.
[18] Han, L., et al. (2014). *Dalton Trans.*, *43*, 8774.
[19] Infantes, L., & Motherwell, S. (2002). *Cryst. Eng. Comm.*, *4*, 454.
[20] Cheruzel, L. E., et al. (2003). *Angew. Chem. Int. Ed.*, *42*, 5452.
[21] Sankaran, P., & Samanta, N. (2003). *Angew. Chem. Int. Ed.*, *42*, 1741.
[22] Sreenivasulu, B., & Vittal, J. J. (2004). *Angew. Chem. Int. Ed.*, *43*, 5769.
[23] Wang, M., Xie, M., Wu, C., & Wang, Y. (2009). *Chem. Commun.*, 2396.
[24] Altomare, A., et al. (1999). *J. Appl. Crystallogr.*, *32*, 115.
[25] Parker, R. J., Spiccia, L., Batten, S. R., Cashion, J. D., & Fallon, G. D. (2001). *Inorg. Chem.*, *40*, 4696.
[26] Li, B., et al. (2013). *Dalton Trans.*, *42*, 2588.