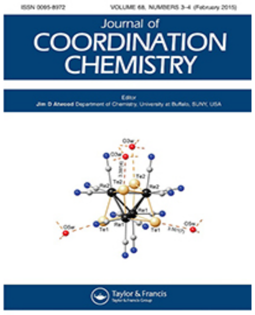


Taylor & Francis
Taylor & Francis Group

Journal of Coordination Chemistry

ISSN: 0095-8972 (Print) 1029-0389 (Online) Journal homepage: http://www.tandfonline.com/loi/gcoo20

Synthesis, structure, and ligand exchange of a copper(II)-based molecular helix with 2,6-pyridinedicarboxylates

Jeonghee Lee, Philjae Kang, Moon-Gun Choi & Hyojong Yoo

To cite this article: Jeonghee Lee, Philjae Kang, Moon-Gun Choi & Hyojong Yoo (2015) Synthesis, structure, and ligand exchange of a copper(II)-based molecular helix with 2,6-pyridinedicarboxylates, Journal of Coordination Chemistry, 68:3, 461-470, DOI: 10.1080/00958972.2014.1000316

To link to this article: http://dx.doi.org/10.1080/00958972.2014.1000316

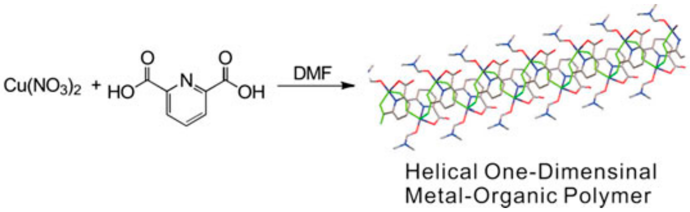
Journal of Coordination Chemistry, 2015
Vol. 68, No. 3, 461–470, http://dx.doi.org/10.1080/00958972.2014.1000316

Synthesis, structure, and ligand exchange of a copper(II)-based molecular helix with 2,6-pyridinedicarboxylates

JEONGHEE LEE†, PHILJAE KANG‡, MOON-GUN CHOI‡ and HYOJONG YOO*†

†Department of Chemistry, Hallym University, Chuncheon, Republic of Korea
‡Department of Chemistry, Yonsei University, Seoul, Republic of Korea

(*Received 18 September 2014; accepted 5 December 2014*)



An one-dimensional (1-D) metal–organic polymer, $[Cu_2(PDA)_2(DMF)_2]_n$ (PDA = 2,6-pyridinedicarboxylate, DMF = dimethylformamide), was synthesized by reaction of copper(II) nitrate hemi(pentahydrate) and 2,6-pyridinedicarboxylic acid in DMF. The complex shows a molecular helix structure consisting of five-coordinate Cu(II) building blocks with distorted square pyramidal geometry. Tridentate chelating PDA, DMF, and an oxygen from the carboxylate of the adjacent Cu(II) building unit are coordinated to the copper(II) center. The weakly coordinated DMF groups in $[Cu_2(PDA)_2(DMF)_2]_n$ easily exchange with a pyridine to generate a pyridine-coordinated non-helical 1-D metal–organic polymer with six-coordinate pseudooctahedral Cu(II) units.

Keywords: Metal–organic polymer; 2,6-Pyridinedicarboxylate; Molecular helix; Ligand exchange

1. Introduction

Helical structures are often found and represent an important class of compounds in nature, examples of which include DNA, RNA, and protein α-helices [1, 2]. The synthesis of polymeric strands by using artificial mimicking of helical biomolecules has attracted attention, as this strategy could provide well-defined geometries for functional devices and materials [3–6]. In particular, helical structures fabricated by coordination of metal ions to organic ligands have opened a new area in supramolecular and polymer chemistry [7–10]. By constructing the unique geometries originating from noncovalent bonding and controlling the ligand–ligand interactions, distinctive helical conformations could have been effectively

---

*Corresponding author. Email: hyojong@hallym.ac.kr

generated [11–14]. More recent publications have been reported on the design of molecular helical structures [15–20].

Metal–organic coordination polymers with 1-, 2-, and 3-D structures are of interest for their applications as materials for molecular magnetism, sensing, and catalysis [21]. To construct such polymeric complexes as molecular helices, bridging and chelating ligands capable of retaining the desired properties and spreading the network have been used. Organic compounds with dicarboxylate have been used for construction of coordination polymers because of their ability to form hybrid polymeric structures through bonding of carboxylates to the metal centers [21–26].

We have tried to synthesize metal–organic hybrid polymers using paramagnetic metal ions and 2,6-pyridinedicarboxylic acid (H_2PDA), an efficient ligand with three coordinating sites, which show interesting structures and could be applied in a variety of areas [27–30, 40–45]. Herein, we report the synthesis and structure of a 1-D metal–organic polymer, $[Cu_2(PDA)_2(DMF)_2]_n$ (PDA = 2,6-pyridinedicarboxylate, DMF = dimethylformamide), by reaction of $Cu(NO_3)_2$ and H_2PDA in DMF. The complex shows a molecular helix chain structure consisting of five-coordinate Cu(II) building blocks with a distorted square pyramidal geometry. This 1-D polymer shows a structural change through ligand exchange. The weakly coordinated DMFs in $[Cu_2(PDA)_2(DMF)_2]_n$ easily exchange with pyridines to generate a pyridine-coordinated non-helical 1-D metal–organic polymer with six-coordinate pseudooctahedral Cu(II) units.

2. Materials and methods

2.1. *Materials*

Copper(II) nitrate hemi(pentahydrate) ($Cu(NO_3)\cdot 2.5H_2O$, ≥98%, Sigma-Aldrich), 2,6-pyridinedicarboxylic acid ($C_7H_5NO_4$, 99%, Sigma-Aldrich), dimethylformamide (DMF, 99.99%, Burdick & Jackson), pyridine (99.8+%, Burdick & Jackson), and dimethylsulfoxide (DMSO, 99.0%, Samchun) were used as received. $CDCl_3$ (99.8%, +0.05% TMS, Cambridge Isotope Laboratories, Inc.) and DMSO-d_6 (99.9%, Cambridge Isotope Laboratories, Inc.) were used as received. Abbreviations used: PDA = 2,6-pyridinedicarboxylate, H_2PDA = 2,6-pyridinedicarboxylic acid.

2.2. *Synthesis of $[Cu_2(PDA)_2(DMF)_2]_n$*

A mixture of $Cu(NO_3)_2\cdot 2.5H_2O$ (69.8 mg, 0.300 mM), H_2PDA (50.1 mg, 0.300 mM), and DMF (6 mL, 78 mM) was sealed in a vial and heated at 120 °C for 3 h, and then cooled slowly to 60 °C. The reaction mixture was kept at 60 °C for another 12 h and then cooled to 25 °C. Blue needle crystals were collected, washed with DMF (2 × 5 mL), and dried. Yield was 94.5% (based on the $Cu(NO_3)_2\cdot 2.5H_2O$ used). Any resonances in ^{1}H NMR were not detected. The existence of strong absorption bands in the FT-IR spectrum of **1** at 1650 cm^{-1} attributes to ν(C=O) and 1363 cm^{-1} to ν(C–O) stretching vibrations. A weak band at 1596 cm^{-1} could be assigned to the C=N group. Anal. Calcd for $C_{10}H_{10}CuN_2O_5$ (%): C, 39.80; H, 3.34; N, 9.28. Found: C, 39.7359; H, 3.4458; N, 9.0514.

2.3. *Ligand exchange reaction of [Cu_2(PDA)$_2$(DMF)$_2$]$_n$ with pyridine; formation of [Cu(PDA)(pyridine)]$_n$ (2)*

Pyridine (0.2 mL, 2.48 mM) was added to a DMSO solution (4 mL) of [Cu_2(PDA)$_2$(DMF)$_2$]$_n$ (121.4 mg, 0.201 mM,) at 25 °C with stirring. Blue crystalline solids started to precipitate within 30 min. The reaction mixture was kept at 25 °C for 12 h, and then the blue crystalline solids were collected, washed with DMF (10 × 5 mL), and dried. Yield was 68.9% (based on the [Cu_2(PDA)$_2$(DMF)$_2$]$_n$ used). The crystals were analyzed by powder X-ray diffraction (PXRD) and single crystal X-ray diffraction, and found to be [Cu(PDA)(pyridine)]$_n$ (**2**) with a 1-D polymeric structure. Complex **2** was also synthesized from the mixture of $Cu(NO_3)\cdot 2.5H_2O$ (46.5 mg, 0.200 mM), H_2PDA (33.4 mg, 0.200 mM), pyridine (1 mL, 12.4 mM), and DMF (4 mL, 52 mM). The reaction mixture was heated and kept at 140 °C for 2 h, and then cooled slowly to 60 °C. The reaction mixture was kept at 60 °C for another 12 h and then cooled to 25 °C. Blue needle crystals were collected, washed with DMF (2 × 5 mL), and dried. Anal. Calcd for $C_{12}H_8CuN_2O_4$ (%): C, 46.83; H, 2.62; N, 9.10. Found: C, 46.7969; H, 2.7394; N, 9.0605.

2.4. *Physical measurements*

All glassware was oven-dried prior to use. ^{1}H NMR spectra were obtained at 300 MHz on a FT NMR Varian Mercury at 303 K. ^{1}H chemical shifts are reported relative to tetramethylsilane. The IR spectrum of the complex from 399 to 4000 cm^{-1} was recorded using KBr pellets on a FT/IR-4200 JASCO spectrometer (JASCO FT/IR-4200 spectrometer).

Table 1. Crystallographic data for [Cu_2(PDA)$_2$(DMF)$_2$]$_n$ (1).

Empirical formula	$C_{10}H_{10}CuN_2O_5$
Formula weight	301.74
Temperature (K)	99.8
Crystal system	Monoclinic
Space group	*C2/c*
a (Å)	22.711(4)
b (Å)	5.9323(9)
c (Å)	17.422(3)
α (°)	90
β (°)	107.285(7)
γ (°)	90
Volume (Å^3)	2241.2(6)
Z	8
ρ_{Calcd} (mg mm^{-3})	1.789
m (mm^{-1})	1.964
F (0 0 0)	1224.0
Crystal size (mm^3)	0.2 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	4.898°–52.266°
Index ranges	$-24 \le h \le 27$, $-7 \le k \le 7$, $-21 \le l \le 21$
Reflections collected	5339
Independent reflections	2136[*R*(int) = 0.1261, *R*(sigma) = 0.0821]
Data/restraints/parameters	2136/153/165
Goodness-of-fit on F^2	1.074
Final *R* indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0582, wR_2 = 0.1617
Final *R* indexes [all data]	R_1 = 0.0686, wR_2 = 0.1840
Largest diff. peak/hole (e Å^{-3})	1.13/−1.65

Thermogravimetric analysis (TGA) was performed on a TA Instruments SDT Q600 analyzer under a nitrogen atmosphere from 18 to 600 °C at a heating rate of 2 °C min^{-1}. PXRD experiments were performed with a RIGAKU Ultima IV diffractometer using Cu Kα radiation (wavelength 1.541 Å) in focused beam and a continuous scan rate of 4° min^{-1} from 3 to 80°. The simulated PXRD pattern was calculated from single crystal X-ray diffraction data by the Mercury 3.3 program. Elemental analyses were performed with Thermo Finnigan Flash EA1112.

2.5. *Single crystal X-ray diffraction analysis of $[Cu_2(PDA)_2(DMF)_2]_n$*

A specimen of suitable size and quality was coated with Paratone oil and mounted on a MiTeGen MicroMount©. Reflection data were collected on a Bruker D8 Venture PHOTON 100 area detector diffractometer with MoKα radiation ($\lambda = 0.71073$ Å). The full sphere of reflection data was collected as ω and φ scan frames with 0.5°/frame and an exposure time of 2 s/frame. Cell parameters were determined and refined by the APEX2 program [35]. Data reduction was performed using SAINT software [36]. The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using SADABS [37]. The structure was solved by direct methods and all nonhydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F^2 using the SHELXTL and Olex 2 GUI programs [38, 39]. Hydrogens were placed at their geometrically calculated positions and refined riding on the corresponding carbons with isotropic thermal parameters.

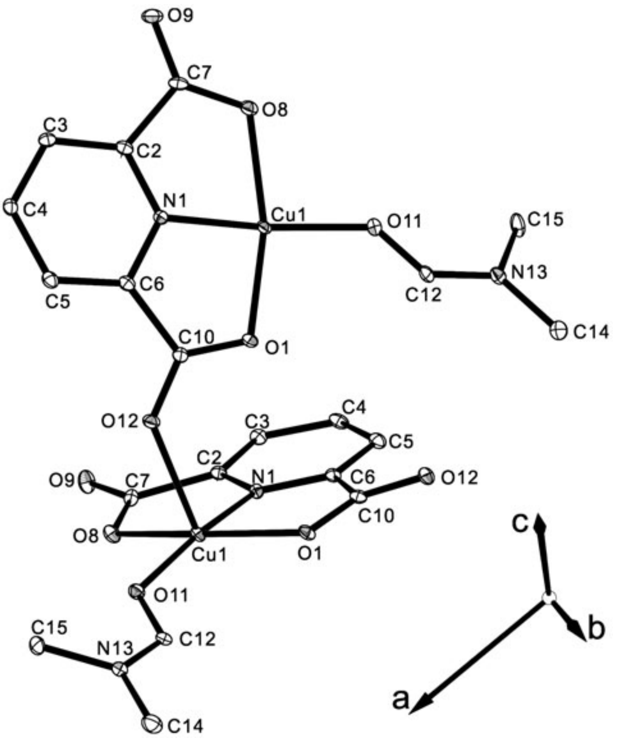
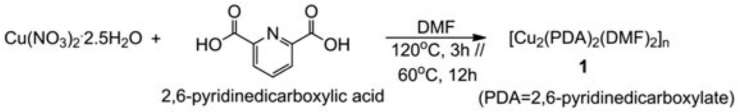


Figure 1. ORTEP drawing of $[Cu_2(PDA)_2(DMF)_2]_n$ (**1**) with 30% probability thermal ellipsoids.

Table 1 lists the cell information, data collection parameters, and refinement data. Tables S1 and S2 (see online supplemental material at http://dx.doi.org/10.1080/00958972.2014.1000316) list the relevant bond distances and angles. Figure 1 is an ORTEP [40] representation of the molecule with 30% probability thermal ellipsoids displayed.

3. Results and discussion

Treatment of $Cu(NO_3)·2.5H_2O$ with 2,6-pyridinedicarboxylic acid (H_2PDA) in DMF for 3 h at 120 °C and 12 h at 60 °C led to formation of $[Cu_2(PDA)_2(DMF)_2]_n$ (**1**) in high yield (94.5%) [equation (1)]. During the reaction, blue crystalline needles precipitated from the reaction mixture. The precipitate was collected, washed with DMF, and dried.



(1)

The solid-state structure of **1** was determined by a single-crystal X-ray diffraction study (figure 1 and table 1). It exhibits a 1-D polymeric chain structure consisting of five-coordinate Cu(II) units with distorted square pyramidal geometry. The nitrogen from

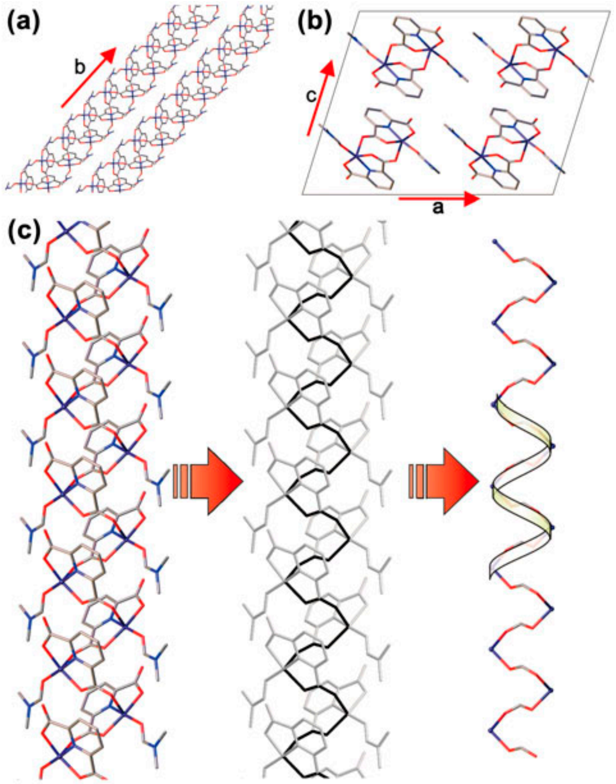


Figure 2. The structural view of 1 along (a) and parallel to the *b* axis (b) of the unit cell; (c) depiction of the core –Cu–O–C–O–Cu– chain of the polymer structure.

PDA is arranged *trans* to the oxygen from DMF (N1–Cu1–O11 = 171.4(1)°). The *trans* O1–Cu1–O8 bond angle is 160.6(1)°, which reflects the constraints of the chelating ligand. A copper (Cu1), three oxygens (O1, O8, and O11), and a nitrogen (N1) are approximately positioned in a plane. The apical site is occupied by an oxygen (O12) from an adjacent PDA. The coordinated DMF is *cis* to the oxygen from the carboxylate of the other Cu(II) unit (O11–Cu1–O12 = 88.2(1)°). Each PDA connects two copper ions: one PDA binds with a copper as a tridentate ligand and the other one via an oxygen from the carboxylate.

The orthogonally twisted connection of two square planes with Cu(II) in the center results in construction of a molecular helical geometry. The structure consists of 1-D chains running along the *b* axis [figure 2(a)]. Two adjacent coppers are linked via carboxylate of a

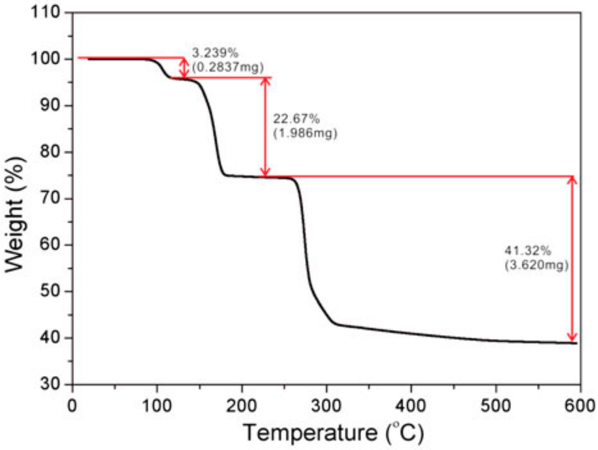


Figure 3. TGA for $[Cu_2(PDA)_2(DMF)_2]_n$ (**1**).

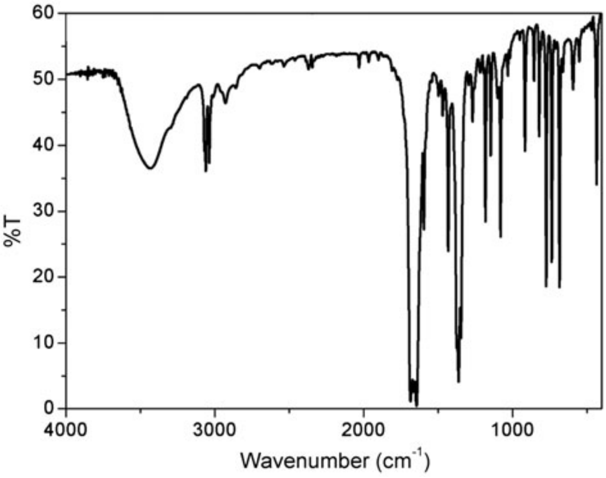


Figure 4. FT-IR spectrum for $[Cu_2(PDA)_2(DMF)_2]_n$ (**1**).

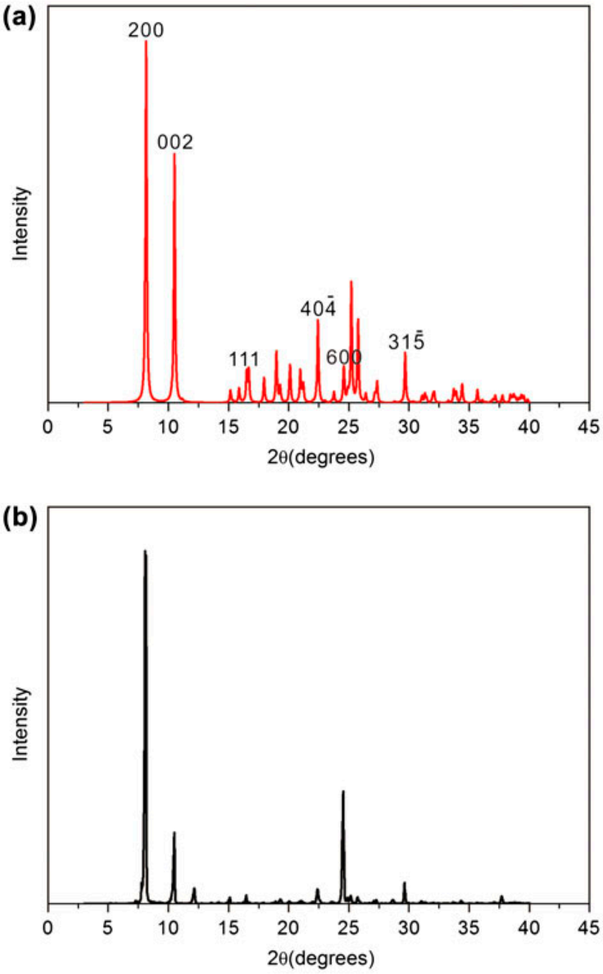
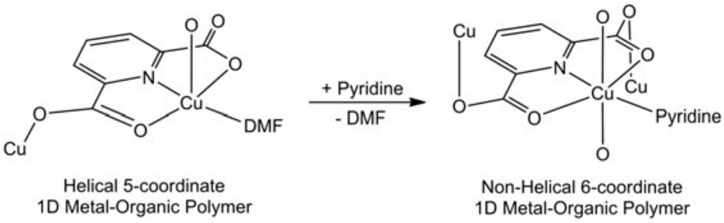


Figure 5. PXRD pattern for $[Cu_2(PDA)_2(DMF)_2]_n$: simulated (a) and experimental (b).

PDA ligand with a resultant Cu–Cu distance of 5.296 Å. In the perpendicular view to the *ac* plane (parallel to the *b* axis), an empty space like a channel in the middle of the structure could be observed, and the Cu building blocks were helically (left-handed) bound and extended to give a polymer chain [figure 2(b)]. Because of the distorted square pyramidal geometry and the unique binding mode of the building blocks, the core –Cu–O–C–O–Cu– chain clearly shows a molecular helix structure [figure 2(c)]. This could be another example of folded molecular helices with metal ion coordinations, which are known to be distinct chain molecules with a secondary structure that mimic biomolecules [1, 2, 7–20, 31–33].

TGA (figure 3), which was performed on crystalline samples of these compounds from 18 to 600 °C, shows a weight loss of 25.91% on equilibrium between 120 and 170 °C corresponding to loss of coordinated DMF (calculated weight ratio: 24.2% for DMF in $[Cu_2(PDA)_2(DMF)_2]_n$). The existence of strong absorption bands in the FT-IR spectrum of



Scheme 1. Ligand exchange of 1 by pyridine.

1 at 1650 cm^{-1} is attributed to *v*(C=O) and 1363 cm^{-1} to *v*(C–O) (figure 4). A weak band at 1596 cm^{-1} could be assigned to C=N. Figure 5(a) is the simulated PXRD pattern expected for the reported structure of **1**. In the experimental PXRD pattern of **1** [figure 5(b)], the basal reflections, 200, 002, and 600, are sharper than that of the basal reflections. There are no significant differences between the observed and the simulated patterns (figure 5).

The DMF molecules in **1** are weakly coordinated and easily exchange with pyridine. Treatment of **1** with excess pyridine (12.3 equiv.) in DMSO at 25 °C leads to formation of blue crystalline solids. The solid-state structure of the crystal, determined by single-crystal X-ray diffraction, showed that this product was an 1-D metal–organic polymer, $[Cu(PDA)(pyridine)]_n$ (**2**) (scheme 1). Complex **2** has been isolated with 68.9% yield. The alternative synthesis and structure determination of **2** were previously reported (figure S1) [34]. The PXRD analysis of **2** showed almost the same pattern as the simulated PXRD pattern calculated from single crystal X-ray diffraction data of the reference [34] (figure S2). Pyridine coordinates to copper, in the *trans* position to nitrogen of PDA, by displacement of DMF from **1**. The Cu(II) building blocks in **2** exhibit six-coordinate pseudooctahedral geometry. The two apical sites are occupied by oxygen from neighboring PDAs, which are chelating copper ions in different units, therefore **2** does not show a helical geometry. The molecular helical 1-D polymer with five-coordinate geometrical units can be directly transformed to a non-helical 1-D polymer structure with six-coordinate units in solution through ligand exchange (scheme 1).

4. Conclusion

A copper(II)-based molecular helix, $[Cu_2(PDA)_2(DMF)_2]_n$, was synthesized by reaction of $Cu(NO_3)_2$ and H_2PDA in DMF. The 1-D polymeric chain consists of five-coordinate Cu(II) building blocks with distorted square pyramidal geometry. Tridentate chelating PDA, DMF, and an oxygen from the carboxylate of the adjacent Cu(II) building unit are coordinated to the copper(II) center. From the solid-state analysis, an empty space like a channel in the middle of the structure was observed, and the Cu units were helically (left-handed) bound and extended to give a polymer chain. This is an unusual example of a molecular helical copper(II)-based polymeric structure with PDA, compared to other polymers with PDA ligands [28–30, 34, 41–46]. This molecular helical 1-D polymer with five-coordinate geometrical building blocks can be directly transformed to another non-helical 1-D polymer with six-coordinate pseudooctahedral Cu(II) units in solution through ligand exchange.

Acknowledgements

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education [NRF-2013R1A1A2057675]; Hallym University Research Fund, 2014 [HRF-201401-010].

References

[1] T.E. Creighton. *Proteins: Structures and Molecular Properties*, 2nd Edn, W.H. Freeman and Co., New York (1993).
[2] W. Saenger. *Principles of Nucleic Acid Structure*, Springer-Verlag, New York (1984).
[3] D.J. Hill, M.J. Mio, R.B. Prince, T.S. Hughes, J.S. Moore. *Chem. Rev.*, **101**, 3893 (2001).
[4] S.H. Gellman. *Acc. Chem. Res.*, **31**, 173 (1998).
[5] S. Hecht, I. Huc. *Foldamers: Structure, Properties, and Applications*, Wiley-VCH, Weinheim (2007).
[6] D.-W. Zhang, X. Zhao, J.-L. Hou, Z.-T. Li. *Chem. Rev.*, **112**, 5271 (2012).
[7] J.-M. Lehn. *Supramolecular Chemistry: Concepts and Perspectives*, Wiley-VCH, Weinheim (1995).
[8] J.-L. Schmitt, A.-M. Stadler, N. Kyritsakas, J.-M. Lehn. *Helv. Chim. Acta*, **86**, 1598 (2003).
[9] M. Albrecht. *Chem. Soc. Rev.*, **27**, 281 (1998).
[10] C. Piguet, G. Bernardinelli, G. Hopfgartner. *Chem. Rev.*, **97**, 2005 (1997).
[11] L. Han, M. Hong. *Inorg. Chem. Commun.*, **8**, 406 (2005).
[12] W.L. Leong, J.J. Vittal. *Chem. Rev.*, **111**, 688 (2011).
[13] M. Albrecht. *Chem. Rev.*, **101**, 3457 (2001).
[14] S. Bala, A. Goswami, S. Sengupta, S. Ganguly, S. Bhattacharya, S. Khanra, R. Mondal. *Cryst. Growth Des.*, **13**, 5068 (2013).
[15] M. Crespo Alonso, M. Arca, F. Isaia, R. Lai, V. Lippolis, S.K. Callear, M. Caricato, D. Pasini, S.J. Coles, M.C. Aragoni. *CrystEngComm*, **16**, 8582 (2014).
[16] H. Zhang, P. Lin, X. Shan, L. Han, S. Du. *CrystEngComm*, **16**, 1245 (2014).
[17] X.-Z. Li, P.-P. Hao, D. Wang, L.-N. Zhu. *CrystEngComm*, **15**, 2800 (2013).
[18] I. Mihalcea, N. Zill, V. Mereacre, C.E. Anson, A.K. Powell. *Cryst. Growth Des.*, **14**, 4729 (2014).
[19] J.-X. Yang, Y.-Y. Qin, J.-K. Cheng, Y.-G. Yao. *Cryst. Growth Des.*, **14**, 1047 (2014).
[20] X. Wang, M.-M. Zhang, X.-L. Hao, Y.-H. Wang, Y. Wei, F.-S. Liang, L.-J. Xu, Y.-G. Li. *Cryst. Growth Des.*, **13**, 3454 (2013).
[21] L.R. MacGillivaray, *Metal-Organic Frameworks: Design and Application*, John Wiley & Sons, Inc. Hoboken, NJ (2010).
[22] L.-N. Jin, Q. Liu, W.-Y. Sun. *CrystEngComm*, **16**, 3816 (2014).
[23] F. Semerci, O.Z. Yeşilel, S. Keskin, C. Darcan, M. Taş, H. Dal. *CrystEngComm*, **15**, 1244 (2013).
[24] T.-W. Tseng, T.-T. Luo, C.-C. Su, H.-H. Hsu, C.-I. Yang, K.-L. Lu. *CrystEngComm*, **16**, 2626 (2014).
[25] B.-M. Kukovec, G.A. Venter, C.L. Oliver. *Cryst. Growth Des.*, **12**, 456 (2012).
[26] M.A. Sharif, G.R. Najafi. *Acta Chim. Slov.*, **60**, 138 (2013).
[27] K.-Y. Choi, H. Ryu, Y.-M. Lim, N.-D. Sung, U.-S. Shin, M. Suh. *Inorg. Chem. Commun.*, **6**, 412 (2003).
[28] Z.-S. Bai, G.-X. Liu, Y. Lu, W.-Y. Sun. *Inorg. Chem. Commun.*, **11**, 513 (2008).
[29] C. Xie, Z. Zhang, X. Wang, X. Liu, G. Shen, R. Wang, D. Shen. *J. Coord. Chem.*, **57**, 1173 (2004).
[30] J.-P. Zhao, Q. Yang, S.-D. Han, J. Han, R. Zhao, B.-W. Hu, X.-H. Bu. *Dalton Trans.*, **42**, 8201 (2013).
[31] E. Yashima, K. Maeda, H. Iida, Y. Furusho, K. Nagai. *Chem. Rev.*, **109**, 6102 (2009).
[32] C. Piguet, G. Bernardinelli, A.F. Williams. *Inorg. Chem.*, **28**, 2920 (1989).
[33] R.F. Carina, G. Bernardinelli, A.F. Williams. *Angew. Chem. Int. Ed. Engl.*, **32**, 1463 (1993).
[34] S.K. Ghosh, J. Ribas, P.K. Bharadwaj. *CrystEngComm*, **6**, 250 (2004).
[35] APEX2 (Version 2013.2-0). *Data Collection Software*, Bruker AXS Inc., Madison, WI (2011).
[36] SAINT (Version 8.30C). *Data Integration Software*, Bruker AXS Inc., Madison, WI (2011).
[37] G.M. Sheldrick. *Version 2.05 SADABS, Program for Absorption Correction with the Bruker SMART System*, Universitat Göttingen, Germany (2011).
[38] G.M. Sheldrick. *SHELXL-93, Program for the Refinement of Crystal Structures*, Universitat Göttingen, Germany (2004).
[39] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann. *J. Appl. Cryst.*, **42**, 339 (2009).
[40] L.J. Farrugia. *J. Appl. Cryst.*, **30**, 565 (1997).
[41] B. Zhao, P. Cheng, Y. Dai, C. Cheng, D.-Z. Liao, S.-P. Yan, Z.-H. Jiang, G.-L. Wang. *Angew. Chem. Int. Ed. Engl.*, **42**, 934 (2003).
[42] M. Frisch, C.L. Cahill. *Dalton Trans.*, **39**, 4679 (2006).
[43] Y.-P. Cai, C.-Y. Su, G.-B. Li, Z.-W. Mao, C. Zhang, A.-W. Xu, B.-S. Kang. *Inorg. Chim. Acta*, **358**, 1298 (2005).

[44] G.-L. Wen, Y.-Y. Wang, P. Liu, C.-Y. Guo, W.-H. Zhang, Q.-Z. Shi. *Inorg. Chim. Acta*, **362**, 1730 (2009).
[45] T.K. Prasad, M.V. Rajasekharan. *Inorg. Chim. Acta*, **363**, 2971 (2010).
[46] X.-L. Wang, J. Luan, Q.-L. Lu, H.-Y. Lin, C. Xu. *J. Organomet. Chem.*, **719**, 1 (2012).