

Synthesis, crystal structure and magnetic properties of two coordination polymers with 4-(4-carboxyphenyl)-4,2':6',4''-terpyridine ligand



Meng-Si Wang^a, Ming-Xing Li^{a,*}, Xiang He^a, Min Shao^b, Zhao-Xi Wang^{a,*}

^a Department of Chemistry, College of Science, Shanghai University, Shanghai 200444, PR China

^b Laboratory for Microstructures, Shanghai University, Shanghai 200444, PR China

ARTICLE INFO

Article history:

Received 15 November 2013

Accepted 19 January 2014

Available online 28 January 2014

Keywords:

Coordination polymer

4-(4-carboxyphenyl)-4,2':6',4''-terpyridine

Crystal structure

Thermal stability

Magnetism

ABSTRACT

Mn^{II} and Co^{II} salts reacting with 4-(4-carboxyphenyl)-4,2':6',4''-terpyridine (4-Hcptpy) in DMF/H₂O afford two complexes, [Mn(4-cptpy)(DMF)(H₂O)₂]_n·n(4-cptpy)·nDMF (**1**) and [Co(4-cptpy)₂(H₂O)₂]_n (**2**). Complex **1** is a 1D ribbon coordination polymer assembled by Mn₂ dimer and tridentate 4-cptpy ligand. The guest 4-cptpy anion is embedded in 3D supramolecular architecture with strong hydrogen bonds. Complex **2** is a 1D linear chain coordination polymer with quadrangled pores. The complex **1** releases H₂O and DMF in 87–150 °C, and the anhydrous [Mn(4-cptpy)]_n·n(4-cptpy) remains thermally stable until 403 °C. Variable temperature magnetic susceptibility study in 2–300 K proves that a weak antiferromagnetic interaction exists in the (μ-O₂CR)₂Mn₂ core.

© 2014 Elsevier B.V. All rights reserved.

The molecular self-assembly, crystal engineering and functional properties of coordination polymers have attracted great interest owing to their intriguing structural motifs and potential applications as functional materials [1–3]. The structural diversity and topology of coordination polymers are attributed to the selection of metal centers, organic ligands and reaction pathways. Much effort has been focused on the purposeful design and controllable synthesis of coordination polymers employing multidentate ligands such as polycarboxylate and N-heterocyclic ligands [4–7]. In contrast to the cohesive terpyridyl moiety of 2-Hcptpy that often acts as a chelating group to assemble mono-nuclear complexes with obvious luminescent properties [8–10], 4-(4-carboxyphenyl)-2,2':6',4''-terpyridine (4-Hcptpy, Scheme 1) contains two side exo-pyridyl groups and trends to construct extended coordination polymers and metal-organic frameworks. The rigid trigonal 4-Hcptpy bifunctional ligand possesses three pyridyl groups and one carboxylic group, which is a valuable multidentate ligand in constructing coordination polymers. However, very few efforts were devoted to 4-Hcptpy complexes to date. In the course of our investigation for coordination polymers and MOFs [11–13], two new one-dimensional coordination polymers, [Mn(4-cptpy)(DMF)(H₂O)₂]_n·n(4-cptpy)·nDMF (**1**) and [Co(4-cptpy)₂(H₂O)₂]_n (**2**), were prepared and structurally characterized. Herein, we report their synthesis, crystal structures, and thermal and magnetic properties.

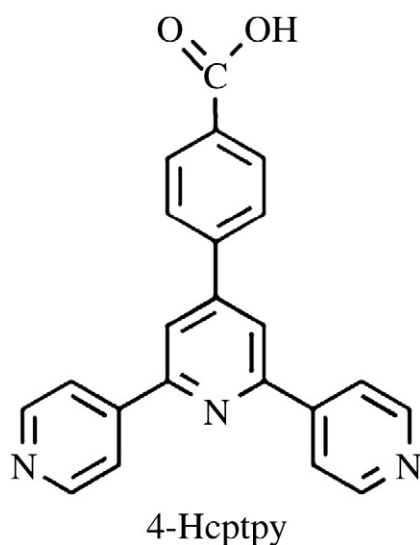
Both complexes were prepared by hydro(solvo)thermal reactions. A mixture of MnCl₂·4H₂O (0.1 mmol), 4-Hcptpy (0.05 mmol), 5 mL DMF and 1 mL water was sealed in a 10 mL Teflon-lined reactor. The reactor

was heated at 100 °C for 72 h. A clear solution without any solid was afforded. Colorless crystals of complex **1** were grown from the solution after one week in 30% yield based on 4-Hcptpy. Anal. Calcd. for C₅₀H₄₆MnN₈O₈ (%): C, 63.76; H, 4.92; N, 11.90. Found: C, 63.31; H, 4.72; N, 11.32. IR (KBr, cm^{−1}): 3417 m, 3074w, 2934w, 1657s, 1595s, 1548s, 1390s, 827s, 788s, 632m. The experimental and simulated PXRD patterns of **1** are in good agreement with each other (Fig. S1, ESI). A mixture of Co(NO₃)₂·6H₂O (0.2 mmol), 4-Hcptpy (0.1 mmol), 1,2,4,5-benzenetetracarboxylic acid (0.1 mmol), 2 mL DMF and 6 mL water was sealed in a 10 mL Teflon-lined reactor. The reactor was heated at 120 °C for 72 h, and then cooled to room temperature at a rate of 10 °C h^{−1}. Several red crystals of complex **2** were obtained. IR (KBr, cm^{−1}): 3394m, 3068w, 1596s, 1528s, 1391s, 1018m, 842s, 829m, 784s, 694m, 632m. The complex **2** can be prepared with a similar procedure except that 1,2,3,4,5,6-cyclohexanhexacarboxylic acid was used instead of 1,2,4,5-benzenetetracarboxylic acid, but the yield is still poor. It was failed to prepare **2** without the addition of benzenetetracarboxylic acid or cyclohexanhexacarboxylic acid. This indicates that the preparation of **2** may be highly influenced by pH value.

The infrared spectra exhibit characteristic 4-cptpy vibration bands in both complexes (Fig. S2). The bands near 3070, 1600, and 1550 cm^{−1} are respectively assigned to the stretching vibrations of C–H, C=C and C=N bonds of 4-cptpy. The bands near 825 and 785 cm^{−1} are designated to the δ(C–H) bending vibrations of pyridyl and phenyl rings. The characteristic absorption band at about 1595 cm^{−1} corresponds to the asymmetric stretching vibration ν_{as}(COO), whereas the band at about 1390 cm^{−1} is attributable to the symmetric stretching vibration ν_s(COO). In addition, the ν(O–H) bands of coordinated water occur at 3417 cm^{−1} for **1** and 3394 cm^{−1} for **2**. In the IR spectrum of **1**, the strong absorption band at 1657 cm^{−1} is ascribed to the stretching vibration of

* Corresponding authors. Tel.: +86 21 66132803; fax: +86 21 66134594.

E-mail addresses: mx_li@mail.shu.edu.cn (M.-X. Li), zxwang@shu.edu.cn (Z.-X. Wang).



Scheme 1. Schematic description of 4-Hcptpy ligand.

carbonyl group ($\text{C}=\text{O}$) in DMF. The absence of characteristic $\nu(\text{COOH})$ band near 1720 cm^{-1} indicates that the carboxyl group is deprotonated for 4-cptpy ligand and guest anion.

X-ray structural analysis [14] revealed that $[\text{Mn}(\text{4-cptpy})(\text{DMF})(\text{H}_2\text{O})_2]_n \cdot n(\text{4-cptpy}) \cdot n\text{DMF}$ (**1**) is a 1D ribbon coordination polymer. As shown in Fig. 1a, the asymmetric unit contains an independent Mn^{II} ion, a 4-cptpy ligand, a DMF and two coordinated H_2O molecules together with a guest 4-cptpy anion and a lattice DMF molecule. Mn1 is six-coordinated with a slight distorted octahedral geometry. Four coordination sites on equatorial plane are occupied by N1, O1, O2, O4 atoms. The axial positions are occupied by water O3 and DMF O5 with a O3-Mn1-O5 bond angle of $175.04(8)^\circ$. The Mn1–O bond distances vary from 2.121(2) to 2.249(2) Å (Table S1, ESI). The Mn–N1 distance is 2.319(2) Å.

The carboxyl group of both 4-Hcptpy is deprotonated. One 4-cptpy acts as a tridentate ligand, while the other 4-cptpy is a guest anion. The tridentate 4-cptpy ligand bonds to three Mn^{II} ions via the bridging carboxyl group and an outer pyridyl group (N1). Another outer pyridyl group and the central pyridyl group are uncoordinated. Mn1 and Mn1A are bridged by two carboxyl groups to form a Mn_2 dimer with a Mn–Mn separation of 5.081(1) Å (Fig. 1b). The binuclear Mn_2 units are interlinked via 4-cptpy spacers to form an extended 1D polymeric ribbon. These 1D ribbons are parallelly arranged to form a 2D supramolecular layer (Fig. 1c). Between adjacent 1D ribbons, there exist face-to-face π – π interactions between central pyridyl rings with a centroid-to-centroid distance of 3.631 Å.

The 2D supramolecular layers formed by the 1D ribbons are further stacked parallelly, which results in a 3D supramolecular architecture as depicted in Fig. 1d. The uncoordinated 4-cptpy anions are sandwiched

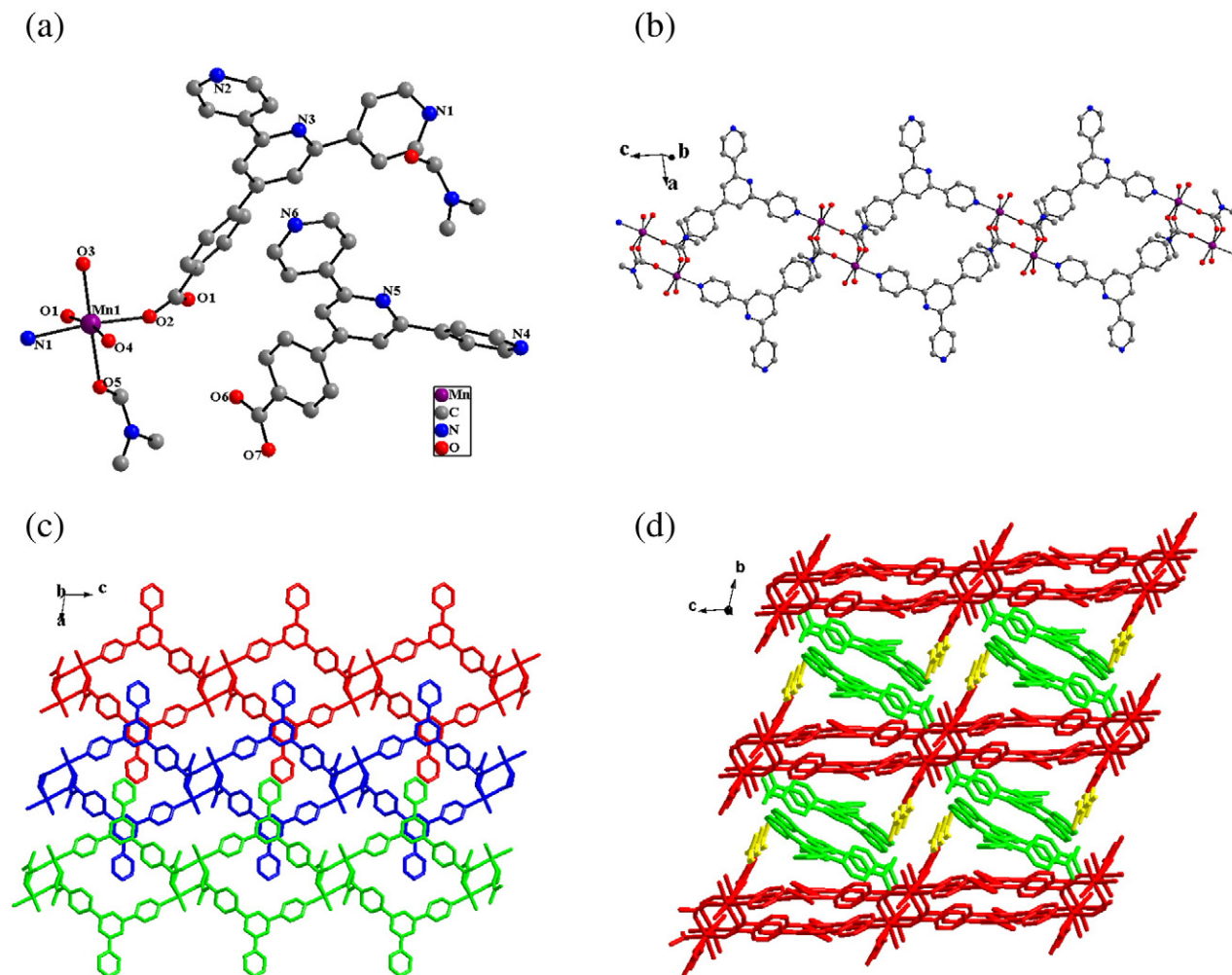


Fig. 1. (a) The asymmetric unit of **1**. (b) The 1D polymeric ribbon. (c) The 2D supramolecular network forming by parallel 1D ribbons. (d) Perspective view of 3D supramolecular network (yellow: lattice DMF, green: 4-cptpy guest anion).

between the 2D supramolecular layers as guest. The guest 4-cptpy links the coordinated water O3 and O4 through four strong hydrogen bonds. The hydrogen bond distances of O(3)–H(3B)...O(6)#1, O(3)–H(3A)...O(6)#4, O(4)–H(4A)...N(4)#5 and O(4)–H(4)...O(7)#4 are 2.703(3), 2.703(3), 2.823(3), 2.600(3) Å, respectively (Table S2, ESI). To date, ten 4-cptpy complexes have been structurally characterized [16–19]. This is the first example that 4-cptpy acts as a guest in supramolecular system. Calculated by the Platon program, there exists larger solvent-accessible void space (304.9 Å³, equal to 13.3% of the cell volume). Within these void spaces, the lattice DMF molecules are perched.

The complex [Co(4-cptpy)₂(H₂O)₂]_n (**2**) is a 1D chain coordination polymer. As shown in Fig. 2a, the asymmetric unit contains an independent Co(II) ion, two 4-cptpy ligands and two coordinated water molecules. Co1 is located in a centrosymmetric *trans* octahedral coordination sphere, coordinated by two carboxyl oxygens and two water oxygens on the equatorial plane, and two pyridyl nitrogens at the axial sites. The bond distances of Co1–N1, Co1–O2 and Co1–O1W are 2.148(9), 2.074(4), 2.152(1) Å, respectively. The bond angles of N1–Co–N1A, O2–Co–O2A and O1W–Co–O1WA are exactly equal to 180°.

The 4-cptpy serves as a bidentate bridging ligand that coordinates to Co1 and Co1A via a monodentate carboxyl group and an out pyridyl group. Another outer pyridyl group and the central pyridyl group are free (Fig. 2b). The terpyridine piece is nearly coplanar, and twists with respect to the phenyl ring (59.1° dihedral angle). Every two 4-cptpy ligands link two cobalt ions to form a quadrangled pore with the size of 14.17 × 7.53 Å². On the basis of the mutual connection between 4-cptpy ligands and cobalt ions, a 1D linear chain structure is built up.

Similar to the packing structure of **1**, the central pyridyl groups between adjacent 1D chains of **2** display face-to-face π – π interaction with a centroid-to-centroid distance of 3.776 Å. Utilizing this weak

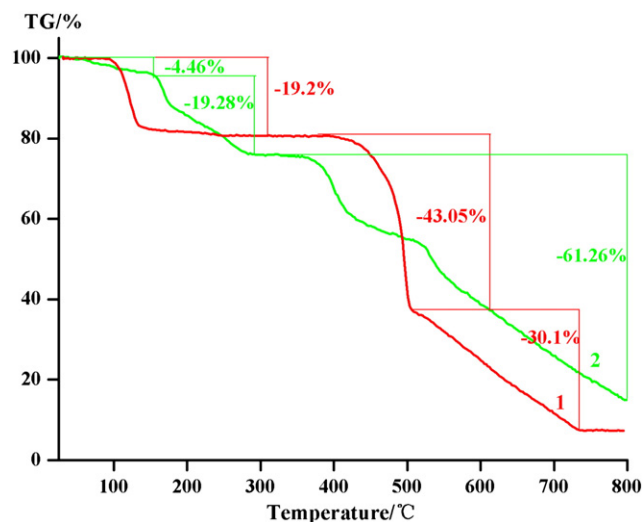


Fig. 3. Thermogravimetric curves of **1** (red) and **2** (green).

binding effect, the 1D chains are parallelly arranged to form a 2D supramolecular layer (Fig. 2c).

Thermogravimetric analyses were performed in 20–800 °C range at a heating rate of 10 °C min^{−1} in air. From the TG–DSC curves of **1** (Figs. 3 and S3), it can be observed that a weight-loss process occurs in 87–150 °C with an endothermic peak at 126 °C, which can be assigned to the release of two coordinated H₂O and two DMF molecules (found, 19.2%; calcd, 19.34%). The anhydrous [Mn(4-cptpy)]_n·n(4-cptpy) remains thermally stable until heated to 403 °C, then exhibits a rapid

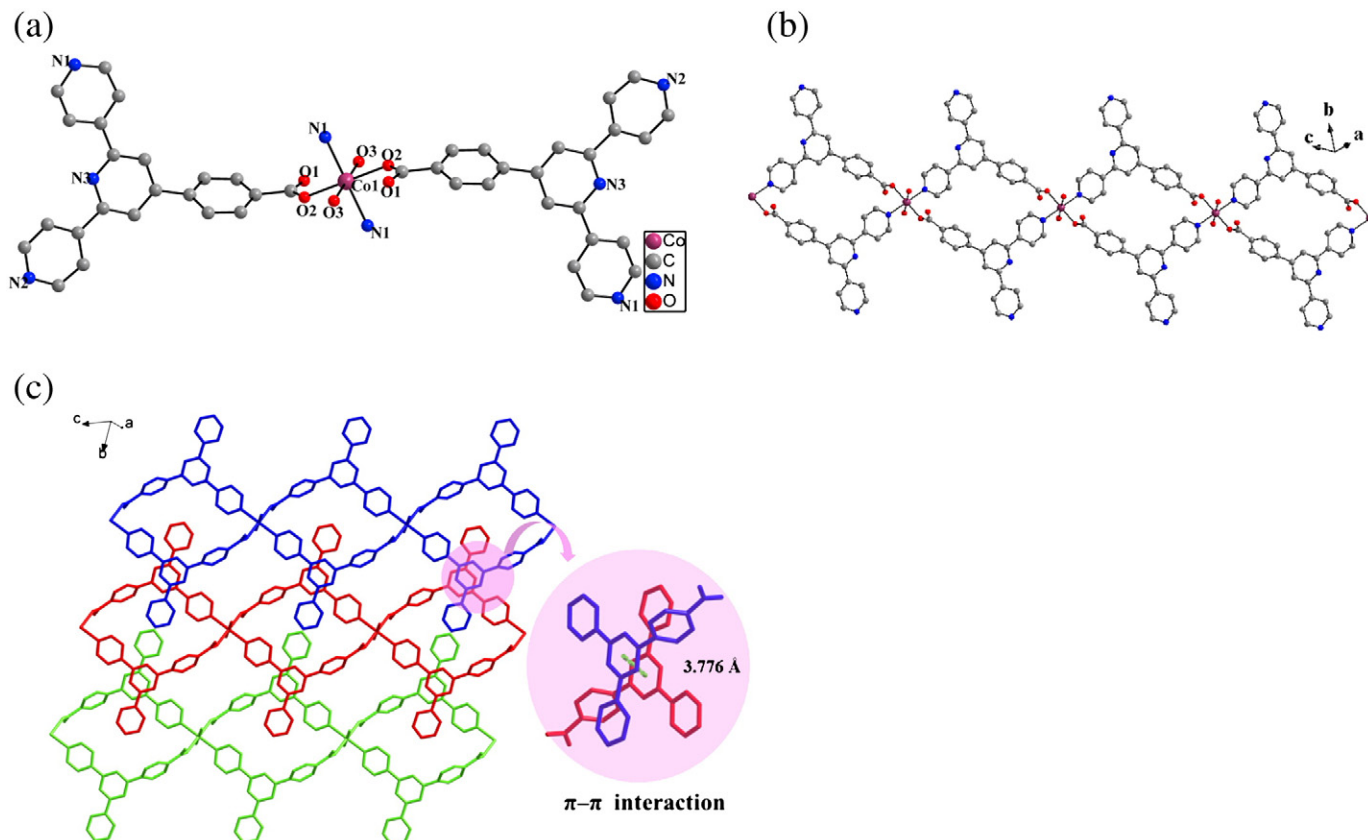


Fig. 2. (a) The asymmetric unit of **2**. (b) The 1D linear chain structure. (c) Perspective view of 2D supramolecular network stacking via π – π interaction.

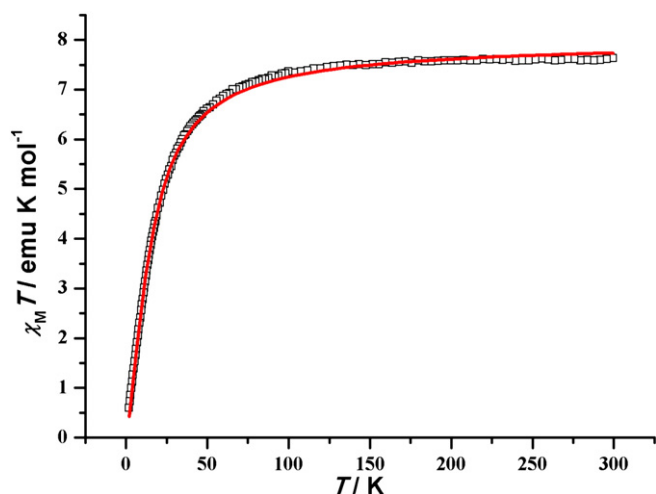


Fig. 4. The plots of $\chi_M T$ vs T for **1**. The solid red line represents the best theoretical fit.

weight-lost process, corresponding to the decomposition process of 4-cptpy. The intermediate would be $[\text{Mn}(\text{ph-COO})_2]$ (found, 43.05%; calcd, 39.01%), which further decomposes in 500–730 °C. The final residue is MnO_2 (found, 7.69%; calcd, 9.23%). Complex **2** shows a weight loss of 4.46% in 50–145 °C assigned to the release of two coordinated water molecules (calcd, 4.50%). Then a successive weight-lost process, accompanying with the decomposition of organic ligand, continues to 800 °C without stop. The final 15.00% residue may be Co_2O_3 (calcd, 10.37%).

The temperature dependence of magnetic susceptibilities of the $\text{Mn}(\text{II})$ complex **1** was measured in 2–300 K range on a crystalline sample with a Quantum Design PPMS-9 magnetometer in a magnetic field of 1000 Oe. A plot of $\chi_M T$ vs T is shown in Fig. 4. The $\chi_M T$ value of carboxyl-bridging Mn^{II}_2 dimer at 300 K is $7.74 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$, which is lower than the only-spin value of Mn^{II}_2 unit ($8.35 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$). Upon cooling the sample, the values of $\chi_M T$ keep smoothly decreasing, which indicate an overall antiferromagnetic coupling in **1**. Considering that the Mn_2 dimer is isolated by larger 4-cptpy ligand and 4-cptpy guest anion, the appropriate magnetic exchange pathway is in the $(\mu\text{-O}_2\text{CR})_2\text{Mn}_2$ core through the bidentate carboxyl bridges.

Due to the magnetic couple that is located at Mn_2 dimer ($\mathbf{S}_1 = \mathbf{S}_2 = 5/2$), a theoretical susceptibility equation based on the spin Hamiltonian ($\mathbf{H} = -2J\mathbf{S}_1 \cdot \mathbf{S}_2$) is employed to evaluate the magnetic exchange constant by fitting the magnetic susceptibility data [20]. This gives the singlet–triplet energy separation value $J = -1.08 \text{ cm}^{-1}$ and $g = 1.91$. The agreement factor R , defined here as $R = \sum(\chi_{\text{obsd}} - \chi'_{\text{calcd}})^2 / \sum(\chi_{\text{obsd}})^2$, is equal to 5.46×10^{-3} . This result proves that a weak antiferromagnetic interaction exists in the $(\mu\text{-O}_2\text{CR})_2\text{Mn}_2$ core.

In conclusion, two coordination polymers were assembled by 4-(4-carboxyphenyl)-4,2':6',4"-terpyridine ligand. $[\text{Mn}(4\text{-cptpy})(\text{DMF})(\text{H}_2\text{O})_2]_n \cdot n(4\text{-cptpy}) \cdot n\text{DMF}$ (**1**) exhibits a 1D ribbon structure construct-

ing from Mn_2 dimer and tridentate 4-cptpy ligand. The guest 4-cptpy anion is embedded in the 3D supramolecular architecture. Variable temperature magnetic susceptibility study proves that a weak antiferromagnetic interaction exists in the $(\mu\text{-O}_2\text{CR})_2\text{Mn}_2$ core.

Acknowledgment

Financially supported by the National Natural Science Foundation of China (21171115, 21203117), and the innovation program (12ZZ089) of Shanghai Municipal Education Commission.

Appendix A. Supplementary material

Crystallographic data for **1**, **2** have been deposited at the Cambridge Crystallographic Data Center, CCDC-971224 for **1** and -943679 for **2**. These data can be obtained from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB21EZ, UK. Supplementary data related to this article can be found online at <http://dx.doi.org/10.1016/j.inoche.2014.01.017>.

References

- [1] T.R. Cook, Y.R. Zheng, P.J. Stang, *Chem. Rev.* 113 (2013) 734.
- [2] H.C. Zhou, J.R. Long, O.M. Yaghi, *Chem. Rev.* 112 (2012) 673.
- [3] S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem. Int. Ed.* 43 (2004) 2334.
- [4] O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim, *Nature* 423 (2003) 705.
- [5] J.P. Zhang, Y.B. Zhang, J.B. Lin, X.M. Chen, *Chem. Rev.* 112 (2012) 1001.
- [6] L.H. Cao, Q.Q. Xu, S.Q. Zang, H.W. Hou, T.C.W. Mak, *Cryst. Growth Des.* 13 (2013) 1812.
- [7] X. Zhu, Q. Chen, Z. Yang, B.L. Li, H.Y. Li, *CrystEngComm* 15 (2013) 471.
- [8] M.W. Cooke, G.S. Hanan, F. Loiseau, S. Campagna, M. Watanabe, Y. Tanaka, *J. Am. Chem. Soc.* 129 (2007) 10479.
- [9] Y. Liu, Z. Chen, J. Ren, X.Q. Zhao, P. Cheng, B. Zhao, *Inorg. Chem.* 51 (2012) 7433.
- [10] Q.R. Wu, J.J. Wang, H.M. Hu, B.C. Wang, X.L. Wu, F. Fu, D.S. Li, M.L. Yang, G.L. Xue, *Inorg. Chem. Commun.* 13 (2010) 715.
- [11] P. Yang, M.X. Li, M. Shao, M.S. Wang, S.X. Cao, J.C. Zhang, H.H. Zhang, *Cryst. Growth Des.* 13 (2013) 4305.
- [12] N. Chen, M.X. Li, P. Yang, X. He, M. Shao, S.R. Zhu, *Cryst. Growth Des.* 13 (2013) 2650.
- [13] P. Yang, X. He, M.X. Li, Q. Ye, J.Z. Ge, Z.X. Wang, S.R. Zhu, M. Shao, H.L. Cai, *J. Mater. Chem.* 22 (2012) 2398.
- [14] Crystal data for **1**: $\text{C}_{50}\text{H}_{46}\text{MnN}_8\text{O}_8$, $M_r = 941.89$, triclinic, space group $P-1$, $a = 10.819(2)$, $b = 14.098(3)$, $c = 15.868(4)$ Å, $\alpha = 105.950(3)^\circ$, $\beta = 96.694(3)^\circ$, $\gamma = 93.262(3)^\circ$, $V = 2301.2(9)$ Å³, $Z = 2$, $D_c = 1.359 \text{ g cm}^{-3}$, μ (Mo-K α) = 0.351 mm^{-1} , $F(000) = 982$, $R_1 = 0.0553$, $wR_2 = 0.1250$ for 10206 unique reflections and 620 parameters, $S = 1.014$. Crystal data for **2**: $\text{C}_{44}\text{H}_{32}\text{CoN}_6\text{O}_6$, $M_r = 799.69$, triclinic, space group $P-1$, $a = 7.123(1)$, $b = 10.787(2)$, $c = 13.232(2)$ Å, $\alpha = 66.423(2)^\circ$, $\beta = 82.408(2)^\circ$, $\gamma = 75.213(2)^\circ$, $V = 900.4(2)$ Å³, $Z = 1$, $D_c = 1.475 \text{ g cm}^{-3}$, μ (Mo-K α) = 0.538 mm^{-1} , $F(000) = 413$, $R_1 = 0.0458$, $wR_2 = 0.1088$ for 3984 unique reflections and 259 parameters, $S = 1.009$. Data were collected on a Bruker Smart Apex-II CCD diffractometer. The structures were solved by direct method and refined on F^2 by full-matrix least squares technique with SHELXTL program [15]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located and included at their calculated positions.
- [15] G.M. Sheldrick, SHELXTL Version 6.1, Bruker AXS Inc., Madison, Wisconsin, USA, 2000.
- [16] L. Wen, X. Ke, L. Qiu, Y. Zou, L. Zhou, J. Zhao, D. Li, *Cryst. Growth Des.* 12 (2012) 4083.
- [17] C. Niu, A. Ning, C. Feng, X. Wan, C. Kou, *J. Inorg. Organomet. Polym.* 22 (2012) 519.
- [18] N. Li, Q.E. Zhu, H.M. Hu, H.L. Guo, J. Xie, F. Wang, F.X. Dong, M.L. Yang, G.L. Xue, *Polyhedron* 49 (2013) 207.
- [19] Y.L. Gai, F.L. Jiang, L. Chen, Y. Bu, M.Y. Wu, K. Zhou, J. Pan, M.C. Hong, *Dalton Trans.* 42 (2013) 9954.
- [20] O. Kahn, *Molecular Magnetism*, VCH Publishers Inc., 1993. 114.