LETTER

NJC
www.rsc.org/njc

A novel 3D framework generated by unusual pillared 2D bilayer motifs†

Jian Zhang,[ab] Zhao-Ji Li,[a] Jian-Kai Cheng,[a] Yao Kang,[a] Ye-Yan Qin[a] and Yuan-Gen Yao*[a]

[a] *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, The Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China. E-mail: yyg@fjirsm.ac.cn*
[b] *Graduate School of the Chinese Academy of Sciences, Beijing, 100039, P. R. China*

Received (in Montpellier, France) 15th October 2004, Accepted 5th January 2005
First published as an Advance Article on the web 8th February 2005

A hydrothermally synthesized mixed-ligand molecular solid has been formulated. The X-ray diffraction analysis of a single crystal revealed a novel 3D architecture generated by unusual 2D bilayer motifs linked up by pillars. Three types of channels in one direction are established inside the structure.

Molecular self-assembly has emerged as an attractive approach to the fabrication of new materials.[1] Among these, novel types of structural motifs and three-dimensional (3D) metal-containing coordination polymers with well-defined pores are particularly attractive.[2] As new motifs, several types of bilayer architectures have been fabricated by the assembly of T-shaped[3], non-T-shaped[4] or rectangular building blocks.[5] However, special bilayer structural motifs such as T-shaped layers linked up by metal centers are rare. Furthermore, controlling the assembly of the bilayer motif, and then utilizing linear bidentate ligands, such as pyrazine, as connectors in an attempt to assemble the sheets into a 3D network is still a challenge for today's chemists.[6]

In the construction of new supramolecular frameworks, polycarboxylate coordination polymeric solids are of special interest.[2a] Aromatic or closed-ring aliphatic polycarboxylates (for example, benzene dicarboxylate, benzene tricarboxylate and adamantane tetracarboxylate) have been widely investigated for the design and synthesis of open framework complexes.[7] In this context, the 3,3′,4,4′-benzophenone tetracarboxylate (BPTC) ligand, which has an irregular orientation when coordinated to metals, is a multidentate asymmetric bridging ligand potentially able to produce open lattice species with various structural topologies and large pores, owing to its tetradentate carboxylic arms and its steric bulk. Still, to the best of our knowledge, BPTC transition metal complexes have not been studied so far.[8]

Herein, we report a new type of a mixed-ligand 3D framework, namely $[Co_2(BPTC)(pyz)(H_2O)_4]\cdot H_2O$ (**1**, pyz = pyrazine), which presents a new remarkable 3D architecture generated by unusual pillared 2D bilayer motifs. Three types of channels in one direction are established inside the framework.

Red crystals of compound **1** were hydrothermally synthesized in very high yield (92%) by reacting $Co(NO_3)_2\cdot 6H_2O$ with 3,3′,4,4′-benzophenone tetracarboxylic dianhydride and pyrazine in the presence of Na_2CO_3 at 160 °C. X-Ray powder diffraction analysis of bulk crystals confirmed that they presented a crystallographically pure phase [see curve b in Fig. 4 below]. Single crystal X-ray diffraction analysis reveals that **1** features a bilayer architecture in which two T-shaped layers are integrated by Co(II) centers into a 2D bilayer network; the bilayers are further pillared by pyz ligands into a 3D structure.

As shown in Fig. 1, each BPTC ligand binds to five Co(II) centers through the O donors from the four carboxylate groups. The two phenyl rings in the same BPTC unit are twisted from each other by 58.96°. There are two crystallographically different Co(II) centers in the structure. Each of them has a slightly distorted $[CoNO_5]$ octahedral coordination geometry and exhibits different linking patterns. Co2 atoms are interconnected *via* T-shaped BPTC ligands, forming a 2D sheet (Fig. 2). The Co2 atoms distributed in the 2D sheet are coplanar. Three carboxylate groups from one BPTC ligand are coordinated to three Co2 atoms, respectively, the fourth

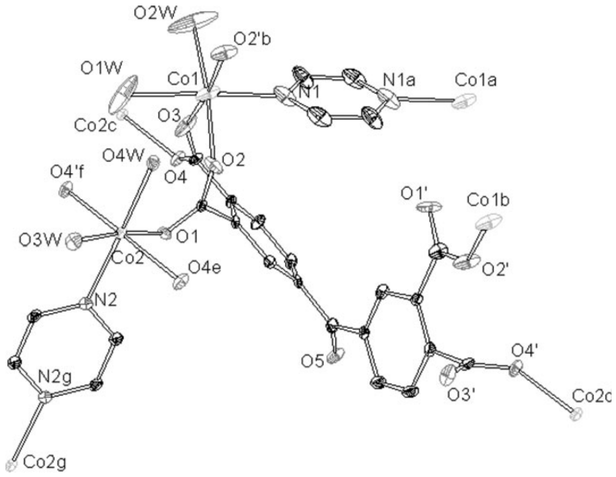

Fig. 1 Crystal structure of **1** showing the atom labelling scheme with 30% probability ellipsoids. Hydrogen atoms and solvent water molecules were omitted for clarify. Selected bond distances (Å) and angles (°): Co(1)–O(2′b) 2.021(5), Co(1)–O(3) 2.034(5), Co(1)–O(2) 2.045(5), Co(1)–N(1) 2.081(8), Co(1)–O(2W) 2.100(7), Co(1)–O(1W) 2.211(9), Co(2)–O(4e) 2.055(4), Co(2)–O(4′f) 2.058(4), Co(2)–O(1) 2.098(4), Co(2)–N(2) 2.127(5), Co(2)–O(3W) 2.139(5), Co(2)–O(4W) 2.143(4), O(3)–Co(1)–O(2) 90.1(2), O(3)–Co(1)–N(1) 93.0(2), O(2)–Co(1)–O(2W) 173.8(4), O(3)–Co(1)–O(1W) 81.3(3), O(2)–Co(1)–O(1W) 89.6(3), N(1)–Co(1)–O(1W) 174.2(3), O(1)–Co(2)–N(2) 86.79(18), O(1)–Co(2)–O(3W) 174.11(18), N(2)–Co(2)–O(3W) 88.0(2), O(1)–Co(2)–O(4W) 99.11(17), N(2)–Co(2)–O(4W) 173.95(19). [Symmetry code: (a) $1-x, 1-y, -z$; (b) $-x, 1-y, -z$; (c) $1+x, y, z$; (d) $x-1, 1+y, z$; (e) $x-1, y, z$; (f) $x+1, y-1, z$; (g) $-x, -y, 1-z$].

---

† Electronic supplementary information (ESI) available: TGA diagram of **1**; stick and space-filling representations of the 3D framework. See http://www.rsc.org/suppdata/nj/b4/b415953e/

DOI: 10.1039/b415953e

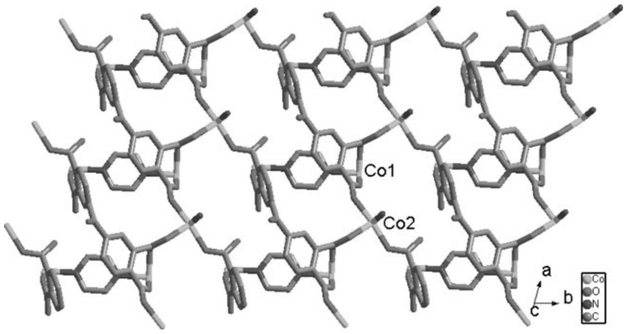

Fig. 2 View of the 2D T-shaped layer in **1**. Two crystallographically independent Co(II) centers exhibit different linking patterns.

being almost perpendicular to the 2D sheet, leading to the generation of a distinct 2D T-shaped layer. Two T-shaped layers are further linked through the O donors of the remaining carboxylate groups and other carboxylate groups on the other side coordinated to Co1 atoms in a face-to-face manner. This results in bilayer galleries, in which planar sheets separately define two types of 1D channels, A and B in Fig. 3. Such a type of molecular bilayer motif is, to the best of our knowledge, unprecedented. Interestingly, Co1 atoms integrated into two adjacent layers are not coplanar. In the parallelogram channel A (crystallographic dimensions 4.64 Å × 7.31 Å, considering the van der Waals radii), the pyz ligands connect symmetrically opposed Co1 atoms, so that they act not only as μ_2 bridges to support the framework, but also as guest molecules to effectively fill the channel. Carboxylate groups link Co1 and Co2 atoms to form the rectangular channel B with dimensions 2.81 Å × 4.38 Å (considering the Van der Waals radii), which is filled by coordinated water molecules. The Co1···Co2 distances separated by the carboxylate groups are 4.763(2) and 5.035(2) Å. Another remarkable feature of **1** is that the pyz ligands also link bilayers together, thus completing the final 3D architecture (Fig. 3). Such a novel 3D open framework can be regarded as a unique molecular "double-floor" directly linked by pillars through covalent bonds. Due to the participation of the pyz ligands, another irregular channel C emerges between the double layers. So far, examples with three types of channels coexisting in one direction are rare.[9]

TGA of **1** shows a first weight loss (found: 13.74%) from 70 to 230 °C, which is attributed to the loss of five guest or bonded water molecules (calcd: 14.01%); the framework $[Co_2(BPTC)(pyz)]_n$ is stable up to 300 °C at which point decomposition starts. Heating-cooling and dehydration-hydration experiments were carried out according to the TGA results and monitored by X-ray powder diffraction technique (XRPD, Fig. 4). Compared to the original crystals, the dehydrated solid obtained by heating crystals of **1** up to 250 °C shows an almost identical XRPD pattern as far as line positions are concerned, but the intensity is weakened (*cf.*curves b and c in Fig. 4). When **1** was heated at 300 °C, some of the characteristic peaks disappeared, but the intensity of the lines could be partially recuperated after this dehydrated solid was immersed in water (*cf.* curves e and f in Fig. 4). This suggests that the dehydration of **1** is reversible. This result illustrates that the main framework of **1**, $[Co_2(BPTC)(pyz)]_n$, which does not lose weight upon heating to 300 °C as shown by the TGA, is retained upon removal of guest and bonded water molecules. The loss of water molecules causes **1** to change color from red to purple. Exposure of a dehydrated sample to air for a few minutes restores the original color, implying that the sample rehydrates very quickly.

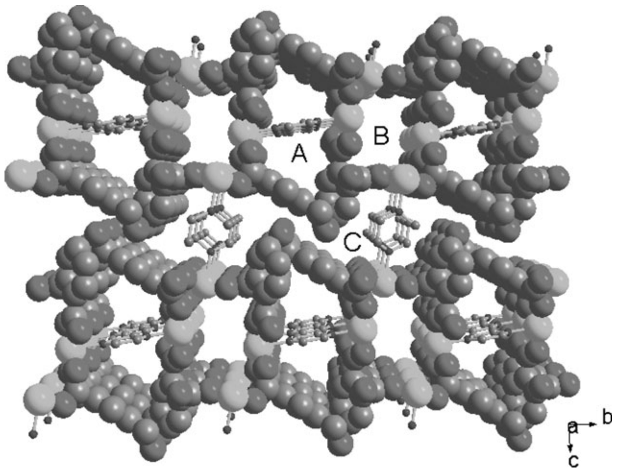

Fig. 3 Space-filling diagram of the 3D framework of **1**. Water molecules included in the channels are omitted for clarity. Co1 atoms link T-shaped layers to form unusual bilayer galleries, which are further pillared up by pyz ligands. Three types of channels in one direction are represented as A, B and C.

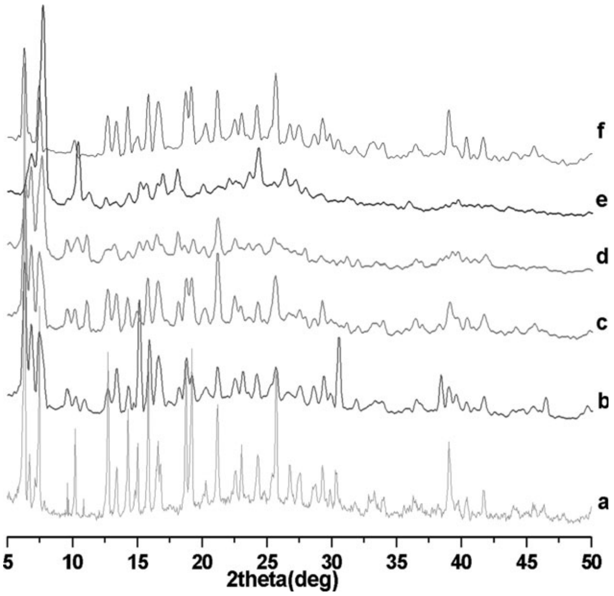

Fig. 4 XRPD patterns for **1**: (a) calculated on the basis of the structure determined by single-crystal X-ray diffraction; (b) taken at room temperature; (c) after heating at 150 °C for 30 min; (d) after heating at 250 °C for 30 min; (e) after heating at 300 °C for 30 min; (f) after rehydration of sample (e) for 24 h.

In summary, using an asymmetric bulky bridging ligand and pillaring spacer, we have successfully constructed a 3D Co coordination polymer with an unusual pillared bilayered structural motif. The structure of this complex provides a unique 3D framework and the results described herein suggest that it might be possible to manipulate and control network morphology by a careful selection of mixed ligands. Further studies, such as magnetic properties of the polymer and self-assembly of the mixed ligands with other metal ions, will be reported elsewhere.

Experimental

Synthesis

A mixture of $Co(NO_3)_2 \cdot 6H_2O$ (0.30 g, 1.0 mmol), Na_2CO_3 (0.10 g, 1.0 mmol), 3,3′4,4′-benzophenone tetracarboxylic dianhydride (0.16 g, 0.5 mmol) and pyrazine (0.08 g, 1.0 mmol) in a 2 : 2 : 1 : 2 molar ratio in 10 ml H_2O was introduced into a Parr Teflon-lined stainless steel vessel (25 cm^3), after which the vessel was sealed and heated to 160 °C. The temperature was held for 3 days and then the mixture was cooled at a rate of 0.5 °C min^{-1} to form red crystals of **1** (yield: 92% based on Co). Anal. calcd for $C_{21}H_{20}Co_2N_2O_{14}$: C, 39.27; H, 3.14; N, 4.36%; found: C, 39.38; H, 3.27, N, 4.33%. IR (KBr pellets, λ/cm^{-1}): 3400 (vs), 3180 (vs), 1656 (m) 1614 (vs), 1553 (vs), 1490 (m), 1424 (s), 1401 (vs), 1303 (m), 1242 (w), 1165 (w), 1083 (w), 850 (w), 823 (w).

X-Ray crystallography

X-Ray intensities from a single crystal of complex **1** were collected with a Siemens Smart CCD diffractometer equipped with graphite-monochromated MoKα radiation ($\lambda = 0.710\ 73$ Å) at 293(2) K. Empirical absorption corrections were applied to the data using the SADABS program.[10] The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL-97 program.[11] All of the nonhydrogen atoms were refined anisotropically. Selected crystal data for **1**‡: $C_{21}H_{20}Co_2N_2O_{14}$, FW = 642.25; triclinic; $P\bar{1}$; $a = 7.3627(14)$, $b = 12.330(3)$, $c = 13.929(2)$ Å, $\alpha = 83.439(8)^\circ$, $\beta = 81.485(7)^\circ$, $\gamma = 72.674(9)^\circ$; $U = 1190.6(4)$ Å^3, $Z = 2$, $D_{calcd} = 1.792$ g cm^{-3}, $\mu = 1.473$ mm^{-1}, $F(000) = 652$, crystal size = 0.20 × 0.10 × 0.07 mm^3. 7636 reflections measured, 4179 unique ($R_{int} = 0.0481$). Final $R = 0.0739$, $wR_2 = 0.1381$ and $S = 1.085$ for 3098 observed reflections with $I > 2\sigma(I)$.

Acknowledgements

This work was supported by the National Natural Science Foundation of China under project No. 20173063, the State Key Basic Research and Development Plan of China (001CB108906), and the NSF of Fujian Province (E0020001).

References

1 J. M. Lehn, *Supramolecular Chemistry, Concepts and Perspectives*, VCH, Weinheim, 1995.

2 (*a*) O. M. Yaghi, H. Li, C. David, D. Richardson and T. L. Groy, *Acc. Chem. Res.*, 1998, **31**, 474; (*b*) O. R. Evans and W. Lin, *Acc. Chem. Res.*, 2002, **35**, 511; (*c*) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629.

3 (*a*) K. N. Power, T. L. Hennigar and M. J. Zaworotko, *New J. Chem.*, 1998, **22**, 177; (*b*) J.-C. Dai, X.-T. Wu, Z.-Y. Fu, C.-P. Cui, S.-M. Hu, W.-X. Du, L.-M. Wu, H.-H. Zhang and R.-Q. Sun, *Inorg. Chem.*, 2002, **41**, 1391; (*c*) Z.-Y. Fu, X.-T. Wu, J.-C. Dai, S.-M. Hu and W.-X. Du, *New J. Chem.*, 2002, **26**, 978; (*d*) C. J. Kepert and M. J. Rosseinsky, *Chem. Commun.*, 1999, 375; (*e*) A. Rujiwatra, C. J. Kepert and M. J. Rosseinsky, *Chem. Commun.*, 1999, 2307; (*f*) S. Kitagawa and M. Kondo, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 1739; (*g*) M. Kondo, T. Yoshitomi, K. Seki, H. Matsuzaka and S. Kitagawa, *Angew. Chem., Int. Ed.*, 1997, **36**, 1725; (*h*) M. J. Zaworotko, *Chem. Commun.*, 2001, 1.

4 J.-C. Dai, S.-M. Hu, X.-T. Wu, Z.-Y. Fu, W.-X. Du, H.-H. Zhang and R.-Q. Sun, *New. J. Chem.*, 2003, **27**, 914.

5 Z.-Y. Fu, X.-T. Wu, J.-C. Dai, L.-M. Wu, C.-P. Cui and S.-M. Hu, *Chem. Commun.*, 2001, 1856.

6 (*a*) X. Y. Huang, J. Li, Y. Zhang and A. Mascarenhas, *J. Am. Chem. Soc.*, 2003, **125**, 7049; (*b*) X. L. Wang, C. Qin, E. B. Wang, Y. G. Li, C. W. Hu and L. Xu, *Chem. Commun.*, 2004, 378.

7 (*a*) H. Li, M. Eddaoudi, M. O'keeffe and O. M. Yaghi, *Nature (London)*, 1999, **402**, 276; (*b*) S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148.

8 Y. Y. Yang, L. Szeto and W.-T. Wong, *Appl. Organomet. Chem.*, 2003, **17**, 958.

9 (*a*) O. V. Dolomanov, D. B. Cordes, N. R. Champness, A. J. Blake, L. R. Hanton, G. B. Jameson, M. Schröder and C. Wilson, *Chem. Commun.*, 2004, 642; (*b*) Q. R. Fang, G. S. Zhu, M. Xue, J. Y. Sun, G. Tian, G. Wu and S. L. Qiu, *J. Chem. Soc., Dalton Trans.*, 2004, 2202.

10 G. M. Sheldrick, *SADABS, Program for area detector adsorption correction*, Institute for Inorganic Chemistry, University of Göttingen, Germany, 1996.

11 *SHELX-TL (Version 5.05)*, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA, 1994.

---

‡ CCDC reference number 251533. See http://www.rsc.org/suppdata/nj/b4/b415953e/ for crystallographic data in .cif or other electronic format.