Two dimensional stair-shaped coordination polymer exhibiting three-dimensional structure with cavities

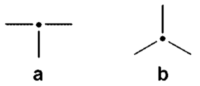
Lei Zhang,[a] Peng Cheng,*[a] Liang-Fu Tang,[a] Lin-Hong Weng,[b] Zong-Hui Jiang,[a] Dai-Zheng Liao,[a] Shi-Ping Yan[a] and Geng-Lin Wang[a]

[a] *Department of Chemistry, Nankai University, Tianjin 300071, P.R. China. E-mail: pcheng@nankai.edu.cn*
[b] *Institute of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, P.R. China*

Received (in Cambridge, UK) 14th January 2000, Accepted 7th March 2000

The crystal structure of {[NaCr(2,2'-bipy)(ox)$_2$]$_2$[bis(1-pyrazolyl)methane]•2H$_2$O}$_n$ reveals the first 2-D stair-shaped architecture which constructs a 3-D network *via* interlayer π–π interactions with guest water molecules present in the cavities.

The synthesis and characterization of 2- or 3-D coordination polymers with well defined pores have been an area of rapid growth and will continue to grow, especially with development of materials of new compositions, predetermined structures and useful properties, *e.g.* catalysis, magnetism, electronics and chemical separation.[1] In recent years the preparation of porous materials whose host frameworks can facilitate the removal/addition of guest molecules has been explored largely owing to their potential applications.[2] In particular, the incorporation of transition metals into coordination polymers is significant in the crystal engineering of novel heterogeneous catalytic systems,[3] as well as non-linear optical, conducting and ferromagnetic materials.[4] Supramolecular synthons are bridged mainly by two types of modules **a** and **b**. Developments in crystal engineering have also shown that hydrogen-bonding and π–π stacking interactions have enormous potential for assembling multi-component inorganic–organic molecules into well organized architectures.[5] It is clear that the strategy of utilizing transition metals with rigid or flexible bifunctional ligands affords an array of new network architectures through self-assembly.[6] However, little attention has been paid to alkaline ions acting as both counter ions and structural elements toward the synthesis of new multidimensional structure.[7] In this contribution, we report the first 2-D stair-shaped network containing hetero-bimetallic Cr^{III}–Na^{I} centers, [NaCr(bipy)(ox)$_2$]$_2$(bpm)·2H$_2$O **1** [bipy = 2,2'-bipyridine, ox = oxalate dianion, bpm = bis(1-pyrazolyl)methane], which forms a 3-D structure containing cavities which can incorporate small molecules.



The reaction of [NaCr(bipy)(ox)$_2$(H$_2$O)]·2H$_2$O and bpm in methanol leads to formation of red plates of [NaCr(bipy)(ox)$_2$]$_2$(bpm)·2H$_2$O, suitable for single X-ray diffraction.† The fundamental tetranuclear unit is shown in Fig. 1. The coordination geometry around the Cr(III) ion is a six-coordinate distorted octahedron, and is similar to those in related complexes.[8] The sodium atoms are also six-coordinate distorted octahedral with larger differences in bond lengths (shown in Fig. 1). Although only the coordinated water molecule has been replaced by the pyrazole nitrogen atom of bpm, the structure has changed significantly. Fig. 2(a) shows that the compound exists as an open railroad framework polymer with channels of 15.0 × 7.3 Å, and shows that the complex molecule is located on a crystallographic two-fold screw axis along the ox bridge ligands. The structure can be represented schematically as a stair-shaped supramolecular architecture as illustrated in Fig. 2(b). This particular supramolecular structure is unprecedented among molecular frameworks.[1b,6c,9]

Within a layer, hydrophilic nitrogen atoms (head or tail) interact with two 1-D inorganic precursors to form two natural hydrophilic–hydrophobic domains. It is interesting that the ligand, bpm, acts as a bidentate bridging ligand rather than as a chelating ligand.[10] In particular, between the layers, the stair-shaped frameworks stack the 2-D structure together *via* interlayer π–π interactions of pyridine rings to form a quasi-3-D structure containing small-pore channels. The narrowest inter-planar distance of the aromatic moieties (bipy) is *ca.* 3.560 Å. The π–π interactions enhance the stability of the complex and result in a higher dimensional structure with the channels parallel to the *b* axis. The effective void size of the channels is 18.6 × 9.3 Å. The cavities are filled with guest water molecules which are hydrogen bonded to oxalato oxygen atoms (2.911 Å) (Fig. 3).

Mixed solvents ($V_{\mathrm{MeOH}}/V_{\mathrm{H_2O}}$ = 1:1, $V_{\mathrm{EtOH}}/V_{\mathrm{H_2O}}$ = 1:1, $V_{\mathrm{EtOH}}/V_{\mathrm{H_2O}}$ = 9:1) were also employed instead of water in the synthesis, but no alcohol molecules were found in the solids obtained.

In conclusion, the design of metal-containing coordination polymers by self-assembly is of great promise. The sizes of the channels offer appreciable potential for guest molecule uptake, and the formation of this type of porous metal–organic

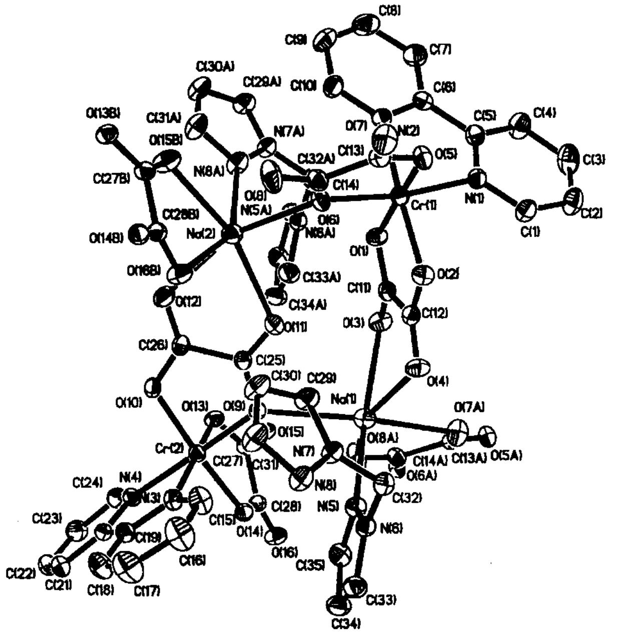


Fig. 1 ORTEP view of the tetranuclear unit of **1** in the crystal. Selected bond lengths (Å): Na1–N5 2.505, Na1–O3 2.424, Na1–O4 2.416, Na1–O7a 2.498, Na1–O8a 2.360, Na1–O9 2.595, Na2–N8a 2.642, Na2–O11 2.362, Na2–O12 2.478, Na2–O15b 2.366, Na2–O16b 2.472, Na2–O6 2.504, Na1–Cr1 5.551, Na1–Cr2 4.202, Na1–Na2 5.521, Na2–Cr1 3.980, Na2–Cr2 5.668, Cr1–Cr2 8.118.

DOI: 10.1039/b000588f

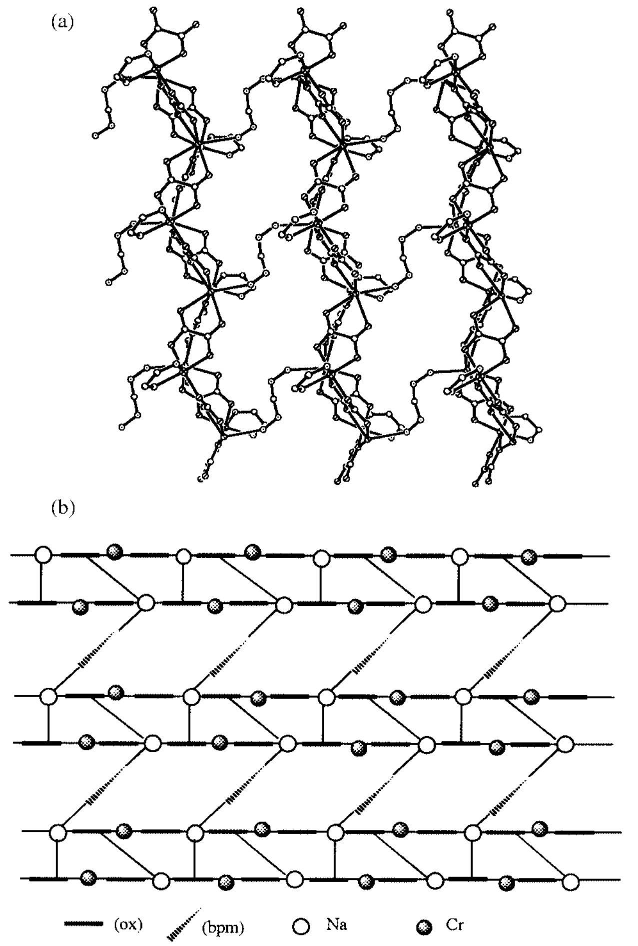


Fig. 2 (a) The helical structure viewed along the crystallographic *ab* plane and (b) a schematic representation of stair-shaped network architecture.

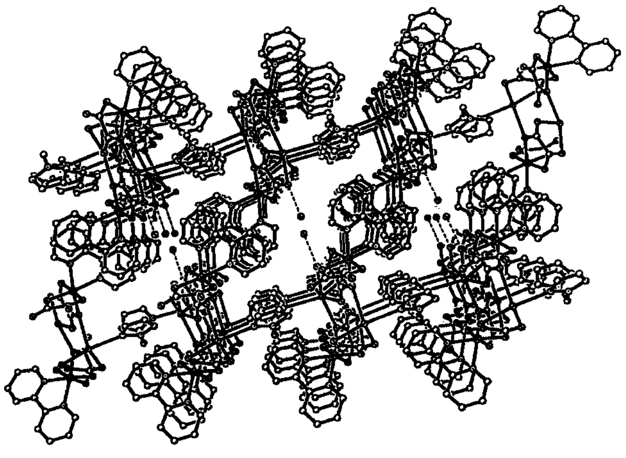


Fig. 3 View of π–π interactions of the pyridyl rings and water molecules in the channels.

compound demonstrates that this aspect of crystal engineering has many potential implications for materials science as new candidates for catalysis or separation processes. We expect that many new functional solid coordination polymers will be synthesized and applied based on these results.

We authors gratefully acknowledge the National Natural Science Foundation of China (29401004 and 29631040) and Ministry of Education of China for support of this work.

Notes and references

† *Crystal data*: $C_{35}H_{28}N_8O_{18}Cr_2Na_2$: M_r = 998.63, triclinic, $P\bar{1}$, a = 9.3366(15), b = 9.5519(15), c = 22.527(4) Å, α = 96.259(3), β = 95.649(3), γ = 95.673(3)°, U = 1975.1(5) Å^3, Z = 2, D_c = 1.679 g cm^{-3}, μ(Mo-K$_\alpha$) = 0.664 mm^{-1}, T = 293(2) K. 11435 Reflections of which 7968 with $I > 2\sigma(I)$ were measured ($2.21 < \theta < 26.44°$) on a Siemens SMART/CCD area detector using the ω-scan mode. The structure was solved by direct methods, and refined by least-squares treatment on F^2 using the SHELXS-97 and the SHELXL-97 programs, R_1 = 0.0442 and R_w = 0.0950 with GOF = 0.973 (R_1 = 0.0783 and R_w = 0.1066 for all data). Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were fixed at calculated positions and refined using a riding model. CCDC 182/1567. See http://www.rsc.org/suppdata/cc/b0/b000588f/ for crystallographic files in .cif format.

1 (*a*) R. Bishop, *Chem. Soc. Rev.*, 1996, 311; (*b*) M. Fujita, Y. J. Kwon, O. Sasaki, K. Yamaguchi and K. Ogura, *J. Am. Chem. Soc.*, 1995, **117**, 7287; (*c*) P. Brunet, M. Simard and J. D. Wuest, *J. Am. Chem. Soc.*, 1997, **119**, 2737; (*d*) O. M. Yaghi, G. Li and H. Li, *Nature*, 1995, **378**, 703; (*e*) D. Venkataraman, G. B. Gardner, S. Lee and J. S. Moore, *J. Am. Chem. Soc.*, 1995, **117**, 11600; (*f*) S. Decurtins, H. W. Schmalle, R. Pellaux, P. Schneuwly and A. Hauser, *Inorg. Chem.*, 1996, **35**, 1451.

2 H. Li, M. Eddaoudi, T. L. Groy and O. M. Yaghi, *J. Am. Chem. Soc.*, 1998, **120**, 8571; C. Janiak, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1431; G. B. Gardner, D. Venkataraman, J. S. Moore and S. Lee, *Nature*, 1995, **374**, 792.

3 I. W. C. E. Arends, R. A. Sheldon, M. Wallau and U. Schuchardt, *Angew. Chem., Int. Ed. Engl.*, 1997, **109**, 1144.

4 A. D. Burrows, C.-W. Chan, M. M. Chowdhry, J. E. McGrady and D. M. P. Mingos, *Chem. Soc. Rev.*, 1995, 329; A. D. Burrows, D. M. P. Mingos, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1996, 97; S. Decurtins, H. W. Schmalle, P. Schneuwly, J. Ensling and P. Gutlich, *J. Am. Chem. Soc.*, 1994, **116**, 9521.

5 S. Kawata, S. R. Breeze, S. Wang, J. E. Greesan and N. P. Raju, *Chem. Commun.*, 1997, 717; R. H. Groeneman, L. R. MacGillivray and J. L. Atwood, *Inorg. Chem.*, 1999, **38**, 208; C. C. Evans, L. Sukarto and D. Ward, *J. Am. Chem. Soc.*, 1999, **121**, 320.

6 (*a*) M. Fujita, Y. J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151; (*b*) S. Subramanian and M. Zaworotko, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2127; (*c*) I. Losier and M. J. Zaworotko, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2779; (*d*) D. M. L. Goodgame, S. Menzer, A. M. Smith and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 574.

7 E. K. Berchin, L. M. Gilby, R. O. Gould, S. G. Harris, S. Parsons and R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.*, 1998, 2657; E. K. Berchin, R. O. Gould, S. G. Harris, S. Parsons and R. E. P. Winpenny, *J. Am. Chem. Soc.*, 1996, **118**, 11293; H. Bock, J.-M Lehn, J. Pauls, S. Holl and V. Krenzel, *Angew. Chem., Int. Ed.*, 1999, **38**, 952.

8 M. C. Muñoz, M. Julve, F. Floret, J. Faus and M. Andruh, *J. Chem. Soc., Dalton Trans.*, 1998, 3125.

9 M. Kondo, T. Yoshitomi, K. Seki, H. Matsuzaka and S. Kitagawa, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1725; H. Gudbjartson, K. Biradha, K. M. Poirier and M. J. Zaworotko, *J. Am. Chem. Soc.*, 1999, **121**, 2599; S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460; M. J. Zaworotko, *Angew. Chem., Int. Ed.*, 1998, **37**, 1211.

10 K. Langenberg, S. R. Batten, K. J. Berry, D. C. R. Hockless, B. Moubaraki and K. S. Murray, *Inorg. Chem.*, 1997, **36**, 5006; L.-F. Tang, L. Zhang, L.-C. Li, P. Cheng, Z.-H. Wang and J.-T. Wang, *Inorg. Chem.*, 1999, **38**, 6326.