DALTON COMMUNICATION

A novel three-dimensional triangular organic–inorganic hybrid network self-assembled by mononuclear [Mn(4,4′-bipyridine)$_2$-(H$_2$O)$_4$]$^{2+}$ cations and rich solvate 4,4′-bipyridine molecules through hydrogen-bonding and π–π interactions†

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The solid compound formulated as [Mn(4,4′-bpy)$_2$-(H$_2$O)$_4$][ClO$_4$]$_2$·(4,4′-bpy)$_4$ (bpy = bipyridine) has been shown by single-crystal structural analysis to be a three-dimensional network with triangular channels, which are constructed by mononuclear [Mn(4,4′-bpy)$_2$(H$_2$O)$_4$]$^{2+}$ cations and 4,4′-bpy molecules through extensive hydrogen-bonds and π–π interactions.

Pronounced interest has recently been focused on the crystal engineering of supramolecular architectures organised by coordinate covalent or supramolecular contacts (such as hydrogen-bonding, π–π interaction *etc.*).[1,2] 4,4′-Bipyridine (4,4′-bpy) is an excellent bridging ligand, and so far a number of one-, two- and three-dimensional infinite metal(I, II or III)–4,4′-bpy frameworks have already been generated.[3] However, of the above-mentioned frameworks, most are generated directly by coordination bonds, or one-dimensional coordination chains are generated first, and are further extended into higher dimensional networks by hydrogen-bonding interactions [Charts 1, 2 and 3],[4] only a few are formed by self-assembly of organic molecules and hydrated metal-ion building blocks.[5] We have been pursuing the synthetic strategies for the preparation of non-interpenetrating open frameworks with variable cavities or channels, in which the rod-like rigid spacers such as 4,4′-bpy, pyrazine and the related species are chosen as building blocks.[6]

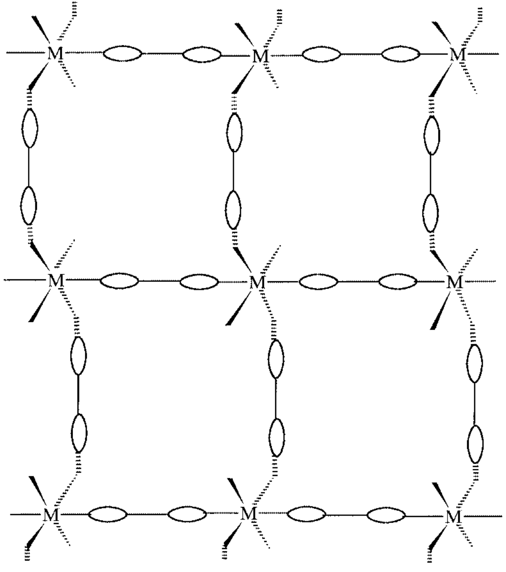

Chart 1

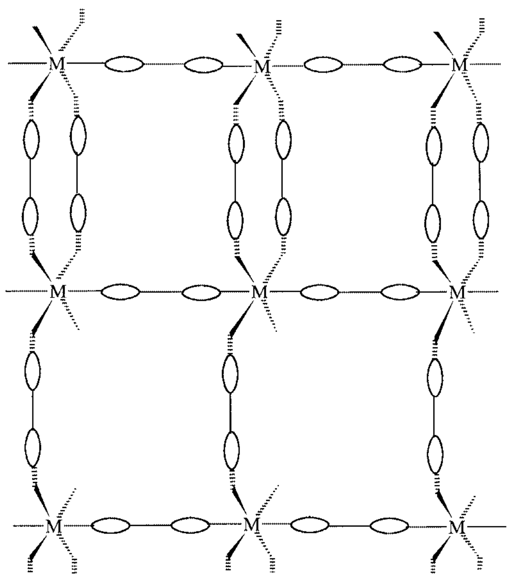

Chart 2

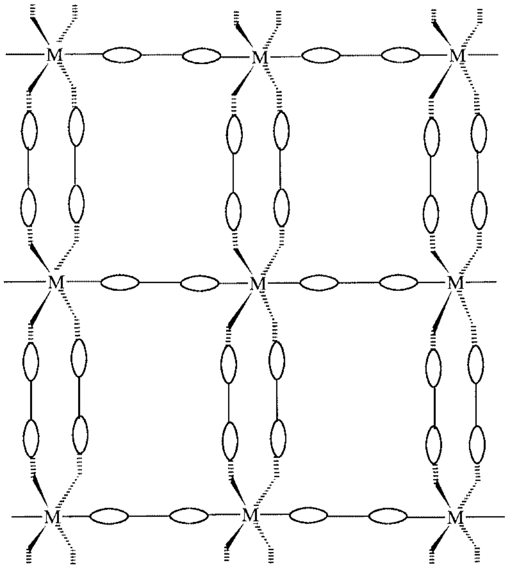

Chart 3

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† *Supplementary Data Available*: rotatable 3-D crystal structure diagram in CHIME format. See http:/www/rsc.org/suppdata/dt/1999/3657/

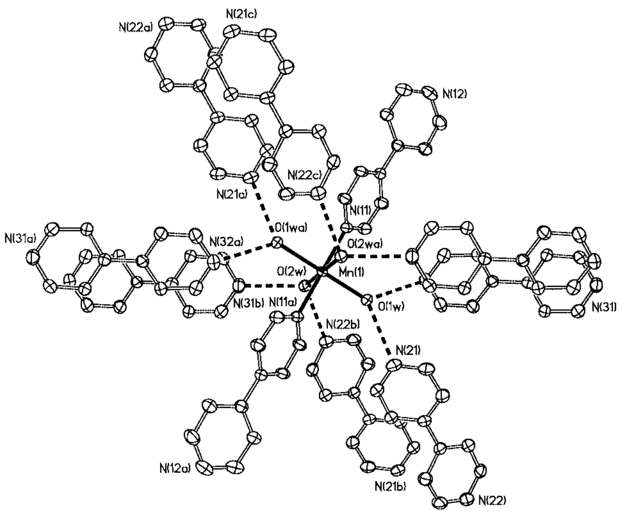

Fig. 1 ORTEP[12] drawing (at 35% probability level) of the mononuclear core in **1**.

In the present work, we report the preparation and crystal structure of a novel three-dimensional triangular organic–inorganic hybrid network self-assembled simultaneously by hydrogen-bonding and π–π interactions, namely $[Mn(4,4'\text{-}bpy)_2(H_2O)_4][ClO_4]_2\cdot(4,4'\text{-}bpy)_4$ **1**.

Complex **1** was synthesised by self-assembly of Mn^{II} ions with 4,4′-bpy ligands, as shown in Chart 4. An ethanolic solution (10 cm^3) of 4,4′-bpy (0.156 g, 1.0 mmol) was added dropwise to a stirred aqueous solution (5 cm^3) of $Mn(ClO_4)_2\cdot 6H_2O$ (0.362 g, 1.0 mmol) at 50 °C for 15 min. The resulting colourless solution was allowed to stand in air at room temperature for 5 days, yielding colourless block crystals (90% yield based on ligand). The elemental analysis confirmed the formula of **1**.‡ It is noteworthy that **1** is, to our knowledge, the compound possessing the highest molar ratio (1 : 6) of 4,4′-bpy and metal. Complex **1** is also the unique product when the molar ratio of Mn^{II} and 4,4′-bpy was changed to 1 : 2 or 1 : 3.

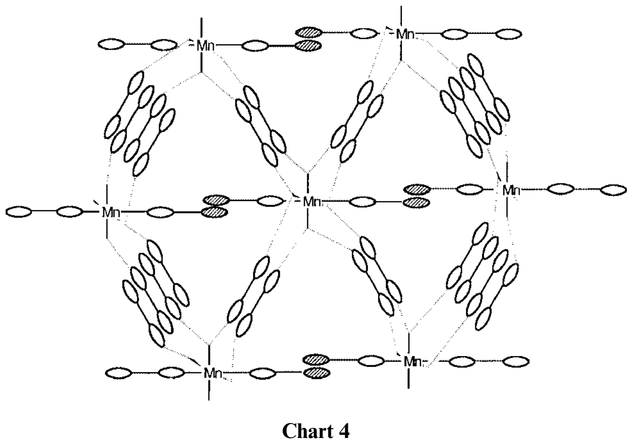

Chart 4

X-Ray crystallography§ has established that complex **1** is made up of mononuclear $[Mn(4,4'\text{-}bpy)_2(H_2O)_4]^{2+}$ cations, solvate 4,4′-bpy molecules and ClO_4^- anions. As shown in Fig. 1, the Mn^{II} atom is, in a slightly octahedral geometry, coordinated to two nitrogen atoms from two different 4,4′-bpy (Mn–N = 2.263(3) Å) and four aqua ligands (Mn–O = 2.174(3)–2.199(2) Å). The divalent cations and the uncoordinated 4,4′-bpy molecules are organised into three-dimensional molecular networks (see Fig. 2) with triangular subunits by π–π interactions and hydrogen-bonds between the solvate 4,4′-bpy and aqua ligands. Each subunit is enclosed by three mononuclear cations and four uncoordinated 4,4′-bpy molecules, each at a conjunctive point and one side of the triangular subunits, respectively, adjacent $Mn^{II}\cdots Mn^{II}$ distances are 14.306 × 14.919 × 15.448 Å, as shown in Chart 4. Each aqua donates two hydrogen bonds with two different 4,4′-bpy molecules (N···O = 2.843(4)–2.885(4) Å, N···O···N = 118.88–130.43°), different from those presented in Charts 1, 2 and 3. The uncoordinated pyridyl ends of 4,4′-bpy ligands from two different mononuclear cations stack with a face-to-face separation of *ca.* 3.55 Å, indicating significant π–π interactions.[7] The pyridyl rings of all 4,4′-bpy molecules are non-coplanar and are twisted by 10.1° and 22.8–32.2° for the coordinated ones and solvate ones, respectively. The inner triangular channels are occupied by the ClO_4^- anions, and each ClO_4^- anion contacts with adjacent 4,4′-bpy molecules, as illustrated in Fig. 3. The C···O distances and C–H···O angles are within the ranges 3.286–3.425 Å and 118.0–172.2°, respectively, indicating significant C–H···O hydrogen bonding interactions, which have recently been documented elsewhere.[8]

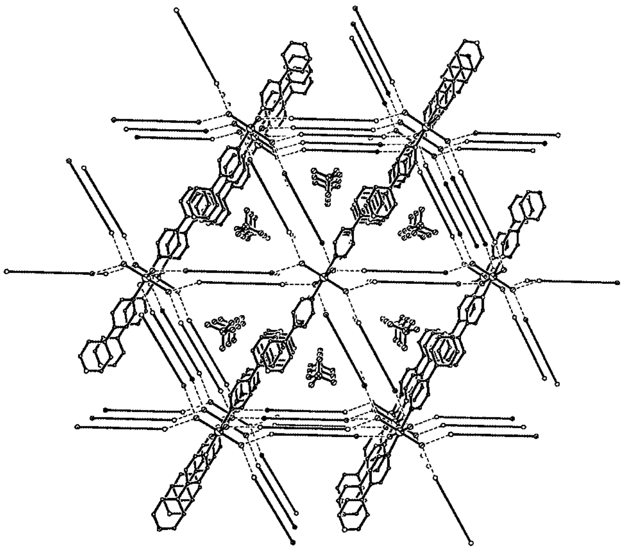

Fig. 2 Top view showing the triangular channels in **1**. The solvate 4,4′-bpy molecules are shown as single bold lines. Hydrogen bonds are represented by broken lines.

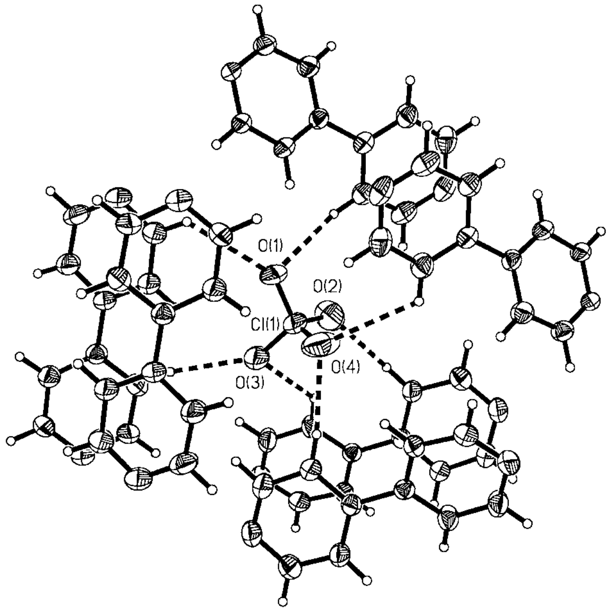

Fig. 3 ORTEP view showing the C–H···O hydrogen bonds among the 4.4′-bpy entities and ClO_4^- ions.

It is noteworthy that complex **1** is, to our knowledge, the first example of three-dimensional metal–4,4′-bpy molecular networks having triangular channels that are sustained by 4,4′-bpy spontaneously through hydrogen-bonding and π–π stacking interactions, although other metal–4,4′-H_2bpy networks with hydrogen-bonding have been intensively investigated.[4] The isolation of **1** and other organic–inorganic hybrid networks[2] involving hydrogen-bonded water molecules suggests the possibility of constructing molecular frameworks with divalent metal salts and organic molecules under appropriate conditions.

The ESR spectrum (X-band) of **1** in acetonitrile at 40 K is characterised by a broad resonance around $g = 2.0$ that is nearly 3200 G, giving six hyperfine coupling splitting lines. This feature is similar to those of related mononuclear Mn^{II} complexes containing nitrogen atoms.[9]

Acknowledgements

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Notes and references

‡ Anal. Calc. for $C_{60}H_{56}N_{12}MnO_{12}Cl_4$ **1**: C, 57.06; H, 4.47; N, 13.31%. Found: C, 56.98; H, 4.38; N, 13.25%.

§ Crystal data for **1**: $C_{60}H_{56}N_{12}MnO_{12}Cl_4$, $M = 1263.02$, triclinic, space group P-1 (No. 2), $a = 7.822(2)$, $b = 14.306(3)$, $c = 14.919(3)$ Å, $\alpha = 63.78(3)$, $\beta = 87.60(3)$, $\gamma = 81.30(3)°$, $V = 1479.9(6)$ Å^3, $Z = 2$, $D_c = 1.572$ g cm^{-3}, $\mu = 6.95$ cm^{-1}. Data collection ($2.64° \le \theta \le 25.0°$) was performed at 293 K on a Siemens R3m diffractometer (Mo-Kα, $\lambda = 0.71073$ Å). The structure was solved with direct methods (SHELXS-97)[10] and refined with full-matrix least-squares technique (SHELX-97)[11] to final R_1 value of 0.0483 for 395 parameters and 2639 unique reflections with $I \ge 2\sigma(I)$ and wR_2 of 0.1358 for all 5219 reflections. CCDC reference number 186/1653. See http://www.rsc.org/suppdata/dt/1999/3657/ for crystallographic files in .cif format.

1 (*a*) D. Braga, F. Grepioni and G. R. Desiraju, *Chem. Rev.*, 1998, **98**, 1375; (*b*) J. C. M. Rivas and L. Brammer, *New J. Chem.*, 1998, **22**, 1315; (*c*) M. Fujita, Y. J. Kwon, S. Washizu, K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151; (*d*) K. N. Power, T. L. Hennigar and M. J. Zaworotko, *New J. Chem.*, 1998, **22**, 177.

2 (*a*) C. J. Kepert, D. Hesek, P. D. Beer and M. J. Rosseinsky, *Angew. Chem.*, *Int. Ed.*, 1998, **37**, 3158; (*b*) M. Tadokoro, K. Isobe, H. Uekusa, Y. Ohashi, J. Toyoda, K. Tashiro and K. Nakasuji, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 95; (*c*) C. B. Aakeroy, A. M. Beatty and D. S. Leinen, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 1815.

3 See recent reviews for examples, (*a*) O. M. Yaghi, in *Access in Nanoporous Materials*, eds. T. J. Pinnavaia and M. F. Thorpe, Plenum, New York, 1995, p. 111; (*b*) S. R. Batten and R. Robson, *Angew. Chem.*, *Int. Ed.*, 1998, **37**, 1460; (*c*) S. Kitagawa and M. Kondo, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 1735; (*d*) A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby and M. Schröder, *Coord. Chem. Rev.*, 1999, **183**, 117.

4 (*a*) A. J. Blake, S. J. Hill, P. Hubberstey and W. S. Li, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 913; (*b*) L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 1801; (*c*) M.-L. Tong, J.-W. Cai, X.-L. Yu, X.-M. Chen, S. W. Ng and T. C. W. Mak, *Aust. J. Chem.*, 1998, **51**, 637; (*d*) G. D. Munno, D. Armentano, T. Poerio, M. Julve and J. A. Real, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 1813.

5 (*a*) L. J. Barbour, L. R. MacGillivray and J. L. Atwood, *Supramol. Chem.*, 1996, **7**, 167; (*b*) G. R. Lewis and A. G. Orpen, *Chem. Commun.*, 1998, 1873; (*c*) C. V. K. Sharma and M. J. Zaworotko, *Chem. Commun.*, 1996, 2655.

6 (*a*) X.-M. Chen, M.-L. Tong, Y.-J. Luo and Z.-N. Chen, *Aust. J. Chem.*, 1996, **49**, 835; (*b*) M.-L. Tong, X.-M. Chen, X.-L. Yu and T. C. W. Mak, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 5; (*c*) M.-L. Tong, B.-H. Ye, J.-W. Cai, X.-M. Chen and S. W. Ng, *Inorg. Chem.*, 1998, **37**, 2645; (*e*) M.-L. Tong, X.-M. Chen, B.-H. Ye and S. W. Ng, *Inorg. Chem.*, 1998, **37**, 5278; (*f*) M.-L. Tong, S.-L. Zheng and X.-M. Chen, *Chem. Commun.*, 1999, 561; (*g*) M.-L. Tong, X.-M. Chen, B.-H. Ye and L.-N. Ji, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 2237.

7 (*a*) C. A. Hunter and J. K. M Sanders, *J. Am. Chem. Soc.*, 1990, **112**, 5525; (*b*) I. Dance and M. Scudder, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 1039.

8 C. V. Krishnamohan, S. T. Griffin and R. D. Rogers, *Chem. Commun.*, 1998, 215.

9 *NMR*, *NQR*, *EPR and Mössbauer Spectroscopy in Inorganic Chemistry*, ed. R. V. Parish, Ellis Horwood Limited, Chichester, 1990.

10 G. M. Sheldrick, SHELXS-97, *Program for X-ray Crystal Structure Solution*, Göttingen University, 1997.

11 G. M. Sheldrick, SHELXL-97, *Program for X-ray Crystal Structure Refinement*, Göttingen University, 1997.

12 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

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