Letter

A three-dimensional honeycomb-like network constructed with novel one-dimensional S-shaped chains *via* hydrogen bonding and π–π interactions†

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The solid compound formulated as [Cu(4,7-phen)(H_2O)$_3$](ClO_4)$_2$ · (4,7-phen)$_2$ (phen = phenanthroline) has been shown by single-crystal structural analysis to be a three-dimensional network with hexagonal channels, constructed of one-dimensional S-shaped [Cu(4,7-phen)(H_2O)$_3$]$_n^{2n+}$ cationic chains and solvated 4,7-phen molecules, linked through extensive hydrogen bonds and π–π interactions.

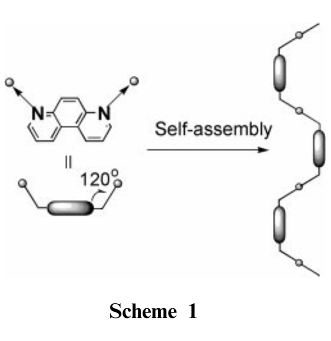
Pronounced interest has recently been focused on the crystal engineering of supramolecular architectures organized by covalent, coordinate or supramolecular bonds (such as hydrogen bonding, π–π interactions *etc*.).[1,2] In particular, strategies directed toward the design of open molecular networks have successfully produced several exotic designer networks.[1–3] Nevertheless, the two-dimensional nature of such architecture has led to interpenetrated and/or offset-stacked structural motifs that prevent the formation of continuous open channel structures.[1,2] Therefore, development of new strategies for the construction of rigid three-dimensional porous architectures has become absolutely essential. We have been pursuing synthetic strategies for the preparation of non-interpenetrating open frameworks with variable size cavities or channels.[4] The 4,7-phen ligand is rigid and capable of binding to transition metal fragments with 120° angles. However, this ligand has not been extensively investigated. Limited examples include a molecular hexagon[5a] and an extended Cu(I) polymeric structure.[5b] In the present work, we report the preparation, crystal structure, and magnetic properties of a novel three-dimensional, honeycomb molecular network, self-assembled by hydrogen-bonding and π–π interactions, namely [Cu(4,7-phen)(H_2O)$_3$](ClO_4)$_2$ · (4,7-phen)$_2$ (**1**).

Complex **1** was synthesized by the self-assembly of Cu(II) ions with 4,7-phen ligands, as shown in Scheme 1. Reaction between 4,7-phen and Cu(II) ions in a 1 : 1 molar ratio in EtOH–H_2O gave the compound [Cu(4,7-phen)(H_2O)$_3$](ClO_4)$_2$ · (4,7-phen)$_2$ (**1**). The elemental analysis and IR spectra confirmed the formula of **1**. It is worth noting that complex **1** is also the only product when the molar ratio of Cu(II) and 4,7-phen was changed to 1 : 2, suggesting the reaction is insensitive to the stoichiometry.

X-Ray crystallographic data reveal that complex **1** is made up of one-dimensional S-shaped [Cu(4,7-phen)(H_2O)$_3$]$_n^{2n+}$ cationic chains [Fig. 1(a)], solvated 4,7-phen molecules, and ClO_4^- anions. As shown in Fig. 1(b), there are two crystallographically distinct Cu(II) ions with almost identical chemical environments. Both Cu(II) ions have square-pyramidal geometry, coordinated to two nitrogen atoms from two different 4,7-phen ligands [Cu(1)–N 2.058(3) and 2.085(3) Å, Cu(2)–N 2.047(3) and 2.085(3) Å] and three aqua ligands [Cu(1)–O 1.937(3)–2.231(3) Å, Cu(2)–O 1.941(3)–2.230(3) Å]. The Cu(II) ions and the 4,7-phen ligands are alternately connected, generating novel one-dimensional S-shaped chains along the *a* axis with an adjacent Cu···Cu intra-chain separation of 7.797 Å [Scheme 1 and Fig. 1(a)].

It is interesting to observe that a hydrogen bond is formed between the *trans*-related aqua ligands in the basal positions and solvated 4,7-phen molecules [O(w)···N 2.656(4)–2.875(4) Å]. This gives rise to two S-shaped hydrogen-bonded chains [Fig. 1(b)] that are located above and below, and run parallel to, the S-shaped [Cu(4,7-phen)(H_2O)$_3$]$_n^{2n+}$ cationic chain. The resultant "triple chain" represents a unique, unprecedented structural feature that has not been previously reported. With face-to-face distances of 3.46–3.75 Å and dihedral angles of 1.68(5)–13.51(6)° among the stacked 4,7-phen rings, such a triple chain is subject to strong π–π interactions.

The most interesting feature of **1** is the three-dimensional honeycomb-like molecular network, formed by the parallel stacking of the adjacent triple chains, running along the *a* axis (Scheme 2 and Fig. 2). The face-to-face separations of 3.45–3.76 Å between the inter-chain 4,7-phen molecules indicate significant π–π interactions. The arrangement and stacking



Scheme 1

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† Electronic supplementary information (ESI) available: experimental and simulated powder X-ray diffraction patterns (Fig. S1) and plots of χ_M^{-1} *vs*. *T* and the effective magnetic moment μ_{eff} *vs*. *T* (Fig. S2) for **1**. See http://www.rsc.org/suppdata/nj/b1/b107655h/

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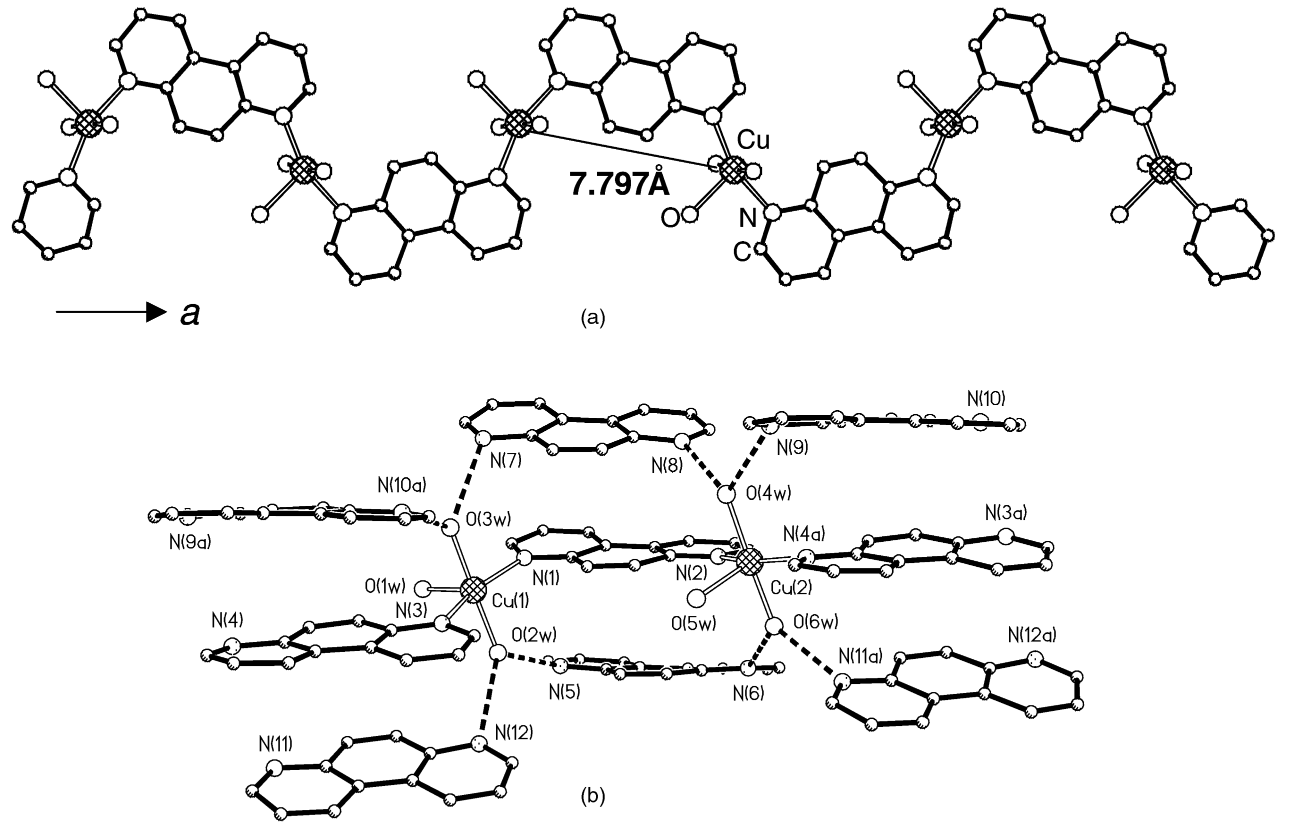
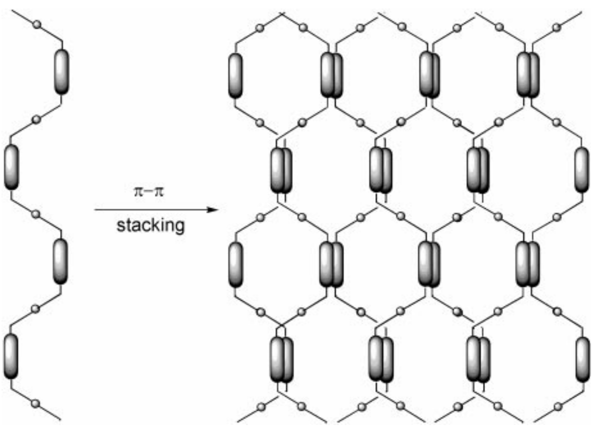


Fig. 1 Perspective view showing the coordination environment. (a) One-dimensional S-shaped $[Cu(4,7\text{-phen})(H_2O)_3]_n^{2n+}$ cationic chain. The Cu···Cu intra-chain distance, 7.797 Å, is indicated on the figure. (b) The triple chain in **1**.

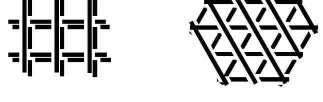
behavior of the linear coordination polymers in **1** are notably different from those found in some recently documented one-dimensional coordination polymers (Scheme 3). The first involved $[Cu(4,4'\text{-bipy})(H_2O)_3(SO_4)]\cdot 2H_2O$, in which the chains in the adjacent layers were arranged in a cross-like fashion at the midpoints of the 4,4′-bipy ligands, resulting in a three-dimensional supramolecular array with rhombic channels running along the *c* axis.[6] The second involved rotating chains in the adjacent layers by 60° to provide helical staircase networks.[7]

The triple chain in **1** is also different from the third type of one-dimensional coordination chain, in which each pair of adjacent polymeric chains is interconnected by hydrogen bonds, resulting in 2D layers.[8] The hexagonal channels with an effective size of *ca.* 6.8 × 5.2 Å^2 [9] in **1** represent 18.1% of the crystal volume[10] and are occupied by the ClO_4^- anions [see Fig. 2(a)]. These anions are hydrogen-bonded to the aqua ligands located at the apical positions [O(w)···O(ClO_4) 2.753(6)–2.774(5) Å] and are also in contact with adjacent 4,7-phen molecules. The C···O distances and C–H···O angles are within the ranges 3.312–3.428 Å and 123.1–151.6°, respectively, indicating significant C–H···O hydrogen bonding interactions, as has been recently documented.[11]

Magnetic susceptibility $\chi_M(T)$ and magnetization $M(H)$ measurements on polycrystalline samples of **1** were performed using a Quantum Design SQUID magnetometer. Powder X-ray diffraction analysis was carried out to ensure that all samples were single-phased (see Fig. S1 in the ESI). In the $\chi_M(T)$ measurements, the temperature was varied from 2 to 350 K and magnetic fields of 5 and 10 kG were applied. $M(H)$ was measured from 0 to 50 kG at 2 K. The $M(H)$ data shows a linear behavior from 0 to 20 kG. The slope then flattens out and reaches a value of 5800 emu mol^{-1} at 50 kG. The temperature dependence of $1/\chi_M(T)$ and the effective magnetic moment μ_{eff}, calculated from $\chi_M T$ for **1**, are shown in Fig. S2 in the ESI. Although an almost trivial Curie behavior is seen in the $1/\chi_M(T)$ *vs.* T plot, more detailed features can be revealed in the μ_{eff} *vs.* T plot. μ_{eff} is 1.75 μ_B at 339 K, which is very close to the value expected for a free Cu^{2+} ion. With decreasing temperature a slight increase in μ_{eff} is seen, indicating a very weak ferromagnetic intra-chain coupling between the Cu^{2+} ions, mediated by the 4,7-phen bridge. μ_{eff} reaches a maximum value near 1.90 μ_B in the temperature range of 40 to 60 K. As temperature decreases from 12 to 2 K, a reduction of 0.13 μ_B in



Scheme 2



Scheme 3

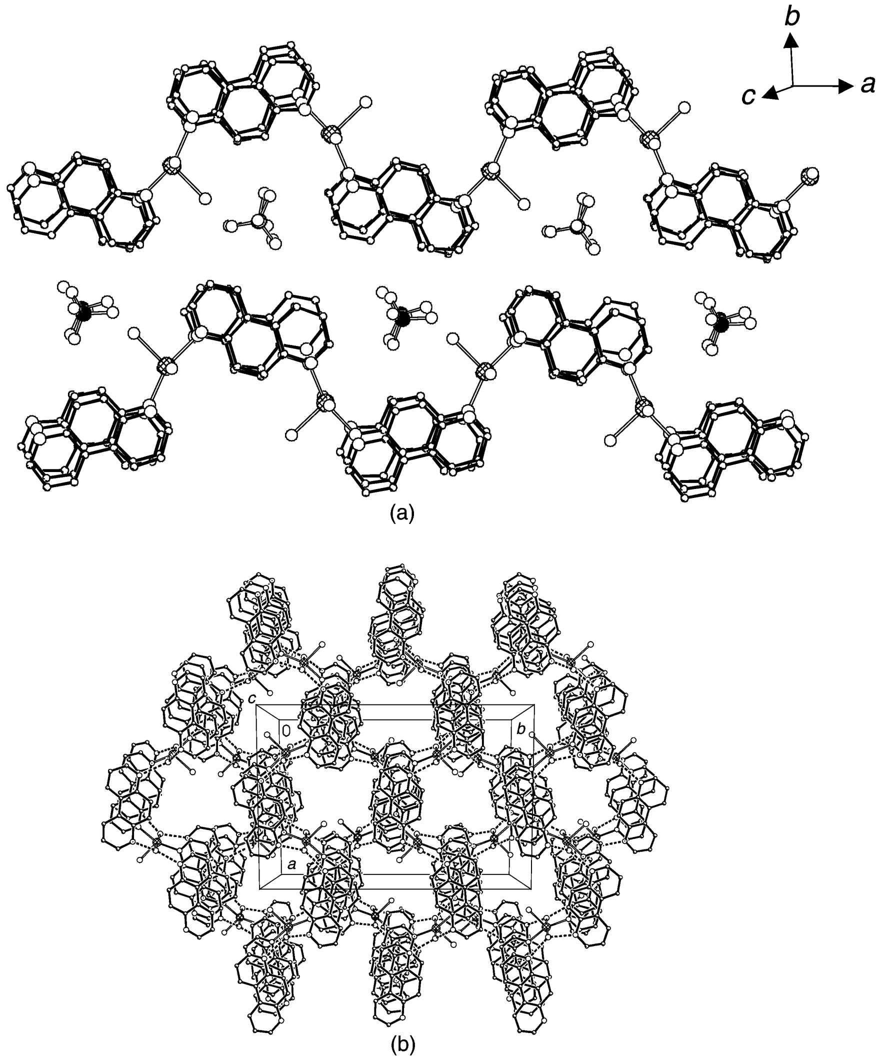


Fig. 2 View showing the stacking pattern of adjacent S-shaped chains. (a) Two parallel triple chains running along the *a* axis. The ClO_4^- anions are shown. (b) Stacking of the triple chains along the *c* axis, leading to a 3D honeycomb topology. The counterions are omitted for clarity.

μ_{eff} is observed. Further studies on the magnetic properties of **1** and other complexes of 4,7-phen are in progress.

Experimental

Synthesis

An ethanol solution (10 ml) of 4,7-phen (0.180 g, 1.0 mmol) was added dropwise to a stirred aqueous solution (5 ml) of $Cu(NO_3)_2 \cdot 3H_2O$ (0.242 g, 1.0 mmol) at 50 °C over a period of 15 min, then a solution (5 ml) of $NaClO_4$ (0.280 g, 2.0 mmol) was added. The resulting colorless solution was allowed to stand in air at room temperature for several days, yielding green block crystals (90% yield based on ligand). Anal. calc. $C_{36}H_{30}Cl_2CuN_6O_{11}$ (**1**): C, 50.45; H, 3.53; N, 9.80; found: C, 50.32; H, 3.48; N, 9.65%. IR (KBr, cm^{-1}): 3588s, 3181m, 3073m, 1626m, 1584m, 1525w, 1500s, 1442m, 1385vs, 1305s, 1239w, 1144vs, 1113vs, 1085vs, 838s, 795s, 717w, 630s, 565w, 498w, 439w.

X-Ray analyses

The powder diffraction analysis of compound **1** was performed on a Rigaku D/M-2200T automated diffraction system (Ultima$^+$). Measurements were made in a 2θ range of 5–80°. The data were collected at room temperature with a step size of 0.027° and a counting time of 0.6 s per step at the operating power of 40 kV and 40 mA.

Data collection ($3.88° \leqslant \theta \leqslant 26.0°$) for the single crystal X-ray diffraction measurement was performed at 293 K on a Bruker CCD diffractometer (Mo-Kα, $\lambda = 0.71073$ Å). The structure was solved by direct methods and refined with full-matrix least-squares technique (SHELX-97)[12] to a final R_1 value of 0.0487 for 1010 parameters and 7058 unique reflections with $I \geqslant 2\sigma(I)$ and wR_2 of 0.1584 for all 14020 reflections. Crystal data for **1**: $C_{36}H_{30}Cl_2CuN_6O_{11}$, $M = 857.10$, monoclinic, space group $P2_1/c$ (no. 14), $a = 15.246(3)$, $b = 22.372(4)$, $c = 21.359(4)$ Å, $\beta = 100.20(3)°$, $U = 7170(2)$ Å^3, $Z = 8$, $D_c = 1.588$ g cm^{-3}, $\mu = 8.31$ cm^{-1}.

CCDC reference number 172557. See http://www.rsc.org/suppdata/nj/b1/b107655h/ for crystallographic data in CIF or other electronic format.

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Notes and references

1 (*a*) K. T. Holman, A. M. Pivovar, J. A. Swift and M. D. Ward, *Acc. Chem. Res.*, 2001, **34**, 107; (*b*) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keefe and O. M. Yaghi,

Acc. Chem. Res., 2001, **34**, 319; (*c*) M. Fujita, *Chem. Soc. Rev.*, 1998, **27**, 417; (*d*) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629.

2 (*a*) S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460; (*b*) A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby and M. Schröder, *Coord. Chem. Rev.*, 1999, **183**, 117.

3 C. V. K. Sharma, in *Crystal Engineering: From Molecules and Crystals to Materials*, ed. D. Braga and G. Orpen, NATO ASI Series, Kluwer, Dordecht, The Netherlands, 1999, pp. 481–500.

4 (*a*) M.-L. Tong, X.-M. Chen, B.-H. Ye and L.-N. Ji, *Angew. Chem., Int. Ed.*, 1999, **38**, 2237; (*b*) M.-L. Tong, S.-L. Zheng and X.-M. Chen, *Chem. Eur. J.*, 2000, **6**, 3729.

5 (*a*) J. R. Hall, S. J. Loeb, G. K. H. Shimizu and G. P. A. Yap, *Angew. Chem., Int. Ed.*, 1998, **37**, 121; (*b*) S. Lopez and S. W. Keller, *Inorg. Chem.*, 1999, **38**, 1883.

6 M.-L. Tong and X.-M. Chen, *Cryst Eng Comm.*, 2000, **1**.

7 (*a*) M. A. Withersby, A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li and M. Schröder, *Angew. Chem., Int. Ed.*, 1997, **36**, 2327; (*b*) D. Hagrman, R. P. Hammond, R. Haushalter and J. Zubieta, *Chem. Mater.*, 1998, **10**, 2091; (*c*) J. Lu, C. Yu, T. Niu, T. Paliwala, G. Crisci, F. Somosa and A. J. Jacobson, *Inorg. Chem.*, 1998, **37**, 4637; (*d*) M. Kondo, M. Shimamura, S. Noro, T. Yoshitomi, S. Minakoshi and S. Kitagawa, *Chem. Lett.*, 1999, 285.

8 (*a*) X.-M. Chen, M.-L. Tong, Y.-J. Luo and Z.-N. Chen, *Aust. J. Chem.*, 1996, **49**, 835; (*b*) 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; (*c*) A. J. Blake, S. J. Hill, P. Hubberstey and W. S. Li, *J. Chem. Soc., Dalton Trans.*, 1997, 913; (*d*) L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Chem. Soc., Dalton Trans.*, 1997, 1801; (*e*) G. D. Munno, D. Armentano, T. Poerio, M. Julve and J. A. Real, *J. Chem. Soc., Dalton Trans.*, 1999, 1813.

9 The channel dimensions are estimated from the van der Waals radii for carbon (1.70 Å), nitrogen (1.55 Å) and oxygen (1.40 Å).

10 A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, The Netherlands, 1999.

11 (*a*) C. V. Krishnamohan, S. T. Griffin and R. D. Rogers, *Chem. Commun.*, 1998, 215; (*b*) M.-L. Tong, H. K. Lee, X.-M. Chen, R.-B. Huang and T. C W. Mak, *J. Chem. Soc., Dalton Trans.*, 1999, 3657.

12 G. M. Sheldrick, SHELX-97, Program for X-ray Crystal Structure Solution and Refinement, Göttingen University, Germany, 1997.