

Poly[diacquabis(μ_3 -hexamethylenetetramine)[μ_2 -2,2'-(piperazine-1,4-diyl)bis(ethanesulfonato)]disilver(I)]: a three-dimensional pillared-layer framework encapsulating a water chain of (H₂O)₁₂ clusters

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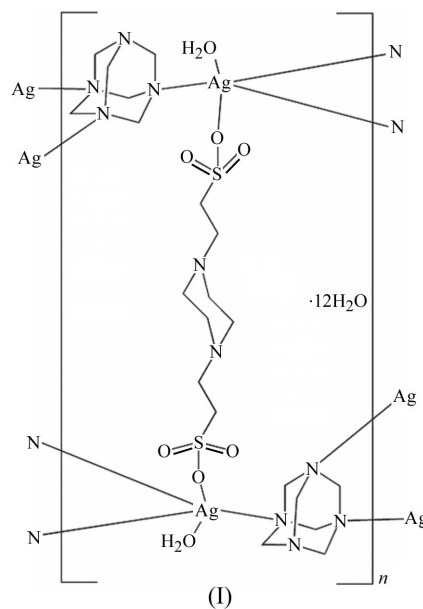
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The title compound, {[Ag₂(C₈H₁₆N₂O₆S₂)(C₆H₁₂N₄)₂(H₂O)₂]-12H₂O}_n, consists of a two-dimensional Ag^I-hexamethylenetetramine (6,3) net pillared by the 2,2'-(piperazine-1,4-diyl)bis(ethanesulfonato) ligand, which lies across a centre of inversion. This compound can also be viewed as a (3,4)-connected topology by considering the hexamethylenetetramine ligand and the Ag^I ion as the three- and four-connected nodes, respectively. There is a one-dimensional channel along the *a* axis accommodating a water chain assembled by the (H₂O)₁₂ clusters.

Comment

Increasing attention is being paid to one-dimensional water chains because of their potential application in the biological transport of water, protons and ions (Ludwig, 2001; Konozo *et al.*, 2002; Roux *et al.*, 1999; Sreenivasulu *et al.*, 2004). Recently, metal-organic frameworks (MOFs) (Eddaoudi *et al.*, 2001), in which the isolated metal centre or the metal clusters are joined through the organic linkers to form an extended structure, have become a promising research field due to the vital roles of MOFs in gas separation, asymmetric catalysis and enantioselective separation. Meanwhile, the rational design of MOFs is conducive to the construction of a channel or cavity in the extended structure, providing a unique opportunity to encapsulate the water chains or water clusters. Among the family of MOFs, pillared-layer structures, with well defined

pores and structural diversity by modification of the pillar module, have been extensively investigated (Ren *et al.*, 2009). We report herein a three-dimensional pillared-layer framework, {[Ag^IL1(H₂O)₂L2]-12H₂O}_n, (I), where L1 is hexamethylenetetramine and L2 is 2,2'-(piperazine-1,4-diyl)bis(ethanesulfonato), with a (3,4)-connected topology accommodating a water chain which is made up of (H₂O)₁₂ clusters in the one-dimensional channel.



The single-crystal X-ray diffraction study reveals that compound (I) is monoclinic and crystallizes in the centrosymmetric space group *P*2₁/*n*. There are one Ag^I ion, one L1 ligand, half an L2 ligand, which lies across a centre of inversion, and seven water molecules in the asymmetric unit. All Ag^I ions show a distorted five-coordinate trigonal-bipyramidal configuration ($\zeta = 0.6135$) (Anthony *et al.*, 1984) with N1, N3ⁱ and N4ⁱⁱ [symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $x - 1, y, z$] atoms from three L1 ligands in equatorial positions and two O atoms in axial positions (Fig. 1). The coordinated

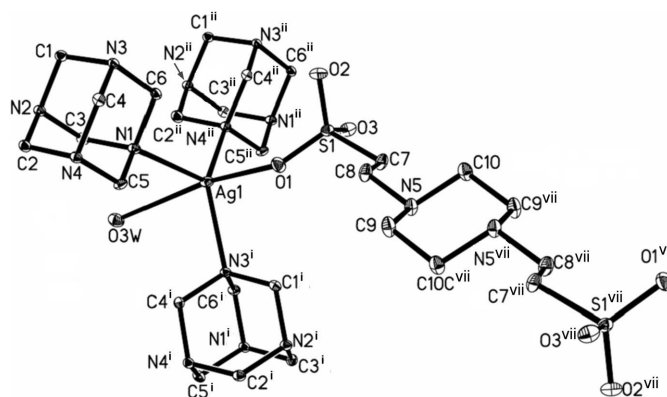
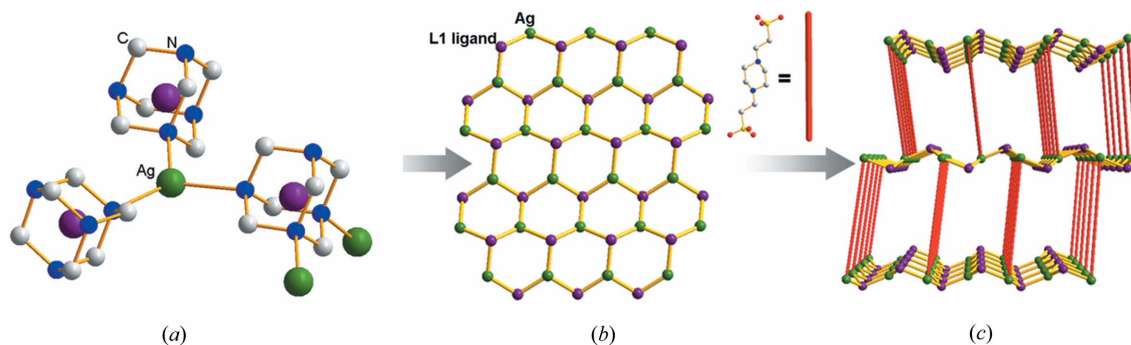


Figure 1
A view of the local coordination of the Ag^I atom in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. All H atoms and isolated water molecules have been omitted for clarity. [Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $x - 1, y, z$; (vii) $-x + 1, -y + 1, -z + 1$.]

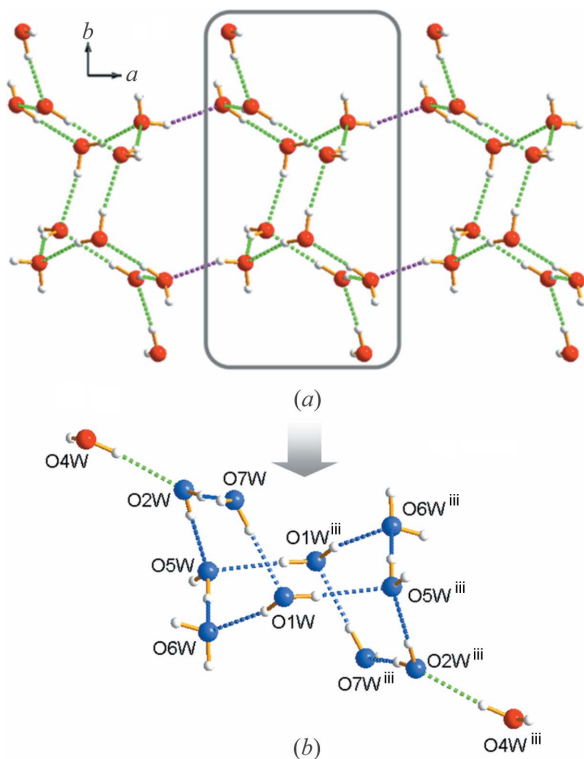
**Figure 2**

(a) The connective environment of the Ag^{I} ion and the L1 ligand; (b) the (6,3) net; (c) a three-dimensional (3,4)-connected topology.

water interacts with the Ag^{I} ion very weakly, with a bond length of 3.077 (2) Å. $\text{Ag}^{\text{I}}-\text{N}$ bonds in the range 2.334 (2)–2.381 (2) Å and the $\text{Ag}^{\text{I}}-\text{O}(\text{sulfonate})$ bond length [2.514 (2) Å; Table 1] are similar to previously reported values (Liu *et al.*, 2009), while $\text{N}-\text{Ag}^{\text{I}}-\text{N}$ angles are in the range 113.10 (8)–130.21 (8)°. All the piperazine rings in the L2 ligands adopt the most stable chair configuration, a finding similar to that of previous work (Sun *et al.*, 2004). Since the Ag^{I} ion connects three L1 ligands and the L1 ligand coordinates with three Ag^{I} ions as well (Fig. 2a), the Ag^{I} -hexamethylenetetramine layer can be viewed as a two-dimensional (6,3) net (Fig. 2b). It is worth noting that the adjacent $\text{Ag}\cdots\text{Ag}$ distances which are similar [5.9827 (4), 6.3421 (4) and 6.3902 (5) Å] show the hexagonal nature of the layer. As shown in Fig. 2(c), pillared by the L2 ligands, compound (I)

can also be presented as a (3,4)-connected topology by considering the L1 ligand and Ag^{I} ion as three- and four-connected nodes, respectively. It is of great interest to note that there is a one-dimensional channel along the *a* axis, providing an available void for the water chain or water cluster.

The fascinating feature of the title compound, (I), is the self-assembly of the $(\text{H}_2\text{O})_{12}$ clusters into a water chain within the one-dimensional channel of the (3, 4)-connected topology. As shown in Fig. 3(a), the $(\text{H}_2\text{O})_{12}$ clusters are composed of the $(\text{H}_2\text{O})_{10}$ clusters and two pendent waters (O4W and O4Wⁱⁱⁱ) (Fig. 3b). Five water molecules (O1W, O2W, O5W, O6W and O7W) and their symmetry-related equivalents form a centrosymmetric decamer, which can also be viewed as two cyclic pentamers bridged across the inversion centre. Besides the cyclic hexamers (O1W, O5W, O6W and their symmetry-related equivalents) with a chair conformation, which have also been found in previous structures containing $(\text{H}_2\text{O})_{12}$ clusters (Song *et al.*, 2007), cyclic pentamers and octamers (O1W, O2W, O5W, O7W and their symmetry-related equivalents) are observed in these clusters. The hydrogen-bonding distances between pairs of O atoms of the water cluster are in the range 2.740 (3)–2.866 (4) Å, resulting in an average of 2.808 Å, while the angles of the hydrogen bonds among $(\text{H}_2\text{O})_{12}$ clusters span the range 150–178° (Table 2). The 14 hydrogen bonds are mainly responsible for the stability of the $(\text{H}_2\text{O})_{12}$ clusters. The individual $(\text{H}_2\text{O})_{12}$ clusters are connected through $\text{O6W}-\text{H62}\cdots\text{O7W}^{\text{vi}}$ hydrogen bonds (symmetry codes as in Table 2), generating an extended water chain which is further anchored into the one-dimensional channel by hydrogen-bonding interactions between the guest water chain and host framework ($\text{O3W}-\text{H31}\cdots\text{O2}^{\text{i}}$, $\text{O3W}-\text{H32}\cdots\text{O3}^{\text{iv}}$, $\text{O4W}-\text{H42}\cdots\text{O3}^{\text{v}}$, $\text{O5W}-\text{H52}\cdots\text{N5}^{\text{v}}$ and $\text{O6W}-\text{H61}\cdots\text{N2}$).

**Figure 3**

(a) A water chain along the *c* axis; (b) the $(\text{H}_2\text{O})_{12}$ clusters; (c) a cyclic pentamer; (d) the simplified structure of the $(\text{H}_2\text{O})_{12}$ clusters. [Symmetry codes: (iii) $-x + 1, -y, -z + 1$.]

Experimental

2,2'-(Piperazine-1,4-diyl)bis(ethanesulfonic acid) (0.5 mmol, 0.15 g) and hexamethylenetetramine (0.5 mmol, 0.07 g) were added to an aqueous solution (10 ml) of silver acetate (0.5 mmol, 0.084 g). After stirring for 15 min, the precipitate was dissolved by dropwise addition of an aqueous solution of NH_3 (14 M). Colourless crystals of complex (I) were obtained by evaporation of the solution for 2 d at room temperature.

Crystal data

[Ag₂(C₈H₁₆N₂O₆S₂)(C₆H₁₂N₄)₂·(H₂O)₂]-12H₂O
M_r = 1048.70
 Monoclinic, *P*2₁/*n*
a = 6.3902 (3) Å
b = 31.1619 (14) Å
c = 10.5428 (5) Å
 β = 93.770 (1)°
V = 2094.85 (17) Å³
Z = 2
 Mo *K*α radiation
 μ = 1.12 mm⁻¹
T = 165 K
 0.41 × 0.28 × 0.19 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
*T*_{min} = 0.200, *T*_{max} = 0.303
 11631 measured reflections
 4128 independent reflections
 3382 reflections with 2σ(*I*)
*R*_{int} = 0.030

Refinement

R [*F*² > 2σ(*F*²)] = 0.030
wR (*F*²) = 0.094
S = 1.14
 4128 reflections
 244 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max}$ = 0.61 e Å⁻³
 $\Delta\rho_{\min}$ = -0.60 e Å⁻³

All H atoms bound to C atoms were refined using a riding model, with a C–H distance of 0.97 Å and *U*_{iso}(H) values of 1.2*U*_{eq}(C) for CH₂ atoms. The water H atoms were located in a difference Fourier map and their positions were initially refined under the application of an O–H bond-length restraint of 0.85 (1) Å. In the final refinement, these H atoms were constrained to ride on their parent atom with *U*_{iso}(H) values set at 1.5*U*_{eq}(O).

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL-Plus (Sheldrick, 2008); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3135). Services for accessing these data are described at the back of the journal.

References

Anthony, W. A. & Rao, T. N. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.
 Bruker (1997). SMART. Version 5.622. Bruker AXS Inc., Madison, Wisconsin, USA.

Table 1

Selected geometric parameters (Å, °).

Ag1–N3 ⁱ	2.334 (2)	Ag1–N1	2.381 (2)
Ag1–N4 ⁱⁱ	2.336 (2)	Ag1–O1	2.514 (2)
N3 ⁱ –Ag1–N4 ⁱⁱ	130.21 (8)	N3 ⁱ –Ag1–O1	86.47 (8)
N3 ⁱ –Ag1–N1	114.09 (8)	N4 ⁱⁱ –Ag1–O1	106.97 (8)
N4 ⁱⁱ –Ag1–N1	113.10 (8)	N1–Ag1–O1	91.88 (8)

Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $x - 1, y, z$.

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O1 <i>W</i> –H11...O6 <i>W</i>	0.85	2.03	2.866 (4)	166
O1 <i>W</i> –H12...O5 <i>W</i> ⁱⁱⁱ	0.85	1.94	2.764 (4)	164
O2 <i>W</i> –H21...O5 <i>W</i>	0.85	1.99	2.836 (4)	178
O2 <i>W</i> –H22...O7 <i>W</i>	0.85	2.03	2.867 (3)	168
O3 <i>W</i> –H31...O2 ⁱ	0.85	2.00	2.818 (3)	163
O3 <i>W</i> –H32...O3 ^{iv}	0.85	1.96	2.797 (3)	169
O4 <i>W</i> –H41...O2 <i>W</i>	0.85	1.93	2.772 (4)	171
O4 <i>W</i> –H42...O3 ^v	0.85	2.04	2.885 (3)	172
O5 <i>W</i> –H51...O6 <i>W</i>	0.85	2.03	2.794 (4)	150
O5 <i>W</i> –H52...N5 ^v	0.85	2.06	2.897 (4)	169
O6 <i>W</i> –H61...N2	0.85	2.05	2.890 (4)	170
O6 <i>W</i> –H62...O7 <i>W</i> ^{vi}	0.85	1.99	2.797 (3)	158
O7 <i>W</i> –H71...O3 <i>W</i>	0.85	2.01	2.841 (3)	167
O7 <i>W</i> –H72...O1 <i>W</i>	0.85	1.89	2.740 (3)	175

Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (iii) $-x + 1, -y, -z + 1$; (iv) $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (v) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (vi) $x + 1, y, z$.

Bruker (1999). SAINT. Version 6.02. Bruker AXS Inc., Madison, Wisconsin, USA.
 Eddaoudi, M., Moler, D. B., Li, H., Chen, B., Reinecke, T. M., O'Keeffe, M. & Yaghi, O. M. (2001). *Acc. Chem. Res.* **34**, 319–330.
 Konoza, D., Yasui, M., King, L. S. & Agre, P. (2002). *J. Clin. Invest.* **109**, 1395–1399.
 Liu, H. Y., Wu, H., Ma, J. F., Yang, J. & Liu, Y. Y. (2009). *Dalton Trans.* **38**, 7957–7968.
 Ludwig, R. (2001). *Angew. Chem. Int. Ed.* **40**, 1808–1827.
 Ren, H., Song, T. Y., Xu, J. N., Jing, S. B., Yu, Y., Zhang, P. & Zhang, L. R. (2009). *Cryst. Growth Des.* **9**, 105–112.
 Roux, B. & MacKinnon, R. (1999). *Science*, **285**, 100–102.
 Sheldrick, G. M. (1996). SADABS. Version 2.03. University of Göttingen, Germany.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Song, H. H. & Ma, B. Qi. (2007). *CrystEngComm*, **9**, 625–627.
 Sreenivasulu, B. & Vittal, J. J. (2004). *Angew. Chem. Int. Ed.* **43**, 5769–5772.
 Sun, D., Cao, R., Bi, W., Li, X., Wang, Y. & Hong, M. (2004). *Eur. J. Inorg. Chem.* pp. 2144–2150.