

catena-Poly[[silver(I)- μ -1,3-bis(4-pyridyl)propane] hemi(naphthalene-1,5-disulfonate) dihydrate]: a three-dimensional metallo-supramolecular sandwich lamellar network

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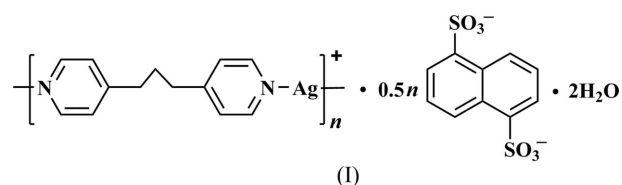
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The title compound, $\{[\text{Ag}(\text{C}_{13}\text{H}_{14}\text{N}_2)](\text{C}_{10}\text{H}_6\text{O}_6\text{S}_2)_{0.5}\cdot 2\text{H}_2\text{O}\}_n$, (I), features a three-dimensional supramolecular sandwich architecture that consists of two-dimensional cationic layers composed of polymeric chains of silver(I) ions and 1,3-bis(4-pyridyl)propane (bpp) ligands, linked by $\text{Ag}\cdots\text{Ag}$ and π - π interactions, alternating with anionic layers in which uncoordinated naphthalene-1,5-disulfonate (nds^{2-}) anions and solvent water molecules form a hydrogen-bonded network. The asymmetric unit consists of one Ag^{I} cation linearly coordinated by N atoms from two bpp ligands, one bpp ligand, one half of an nds^{2-} anion lying on a centre of inversion and two solvent water molecules. The two-dimensional $\{[\text{Ag}(\text{bpp})]^+\}_n$ cationic and $\{[(\text{nds})\cdot 2\text{H}_2\text{O}]^{2-}\}_n$ anionic layers are assembled into a three-dimensional supramolecular framework through long secondary coordination $\text{Ag}\cdots\text{O}$ interactions between the sulfonate O atoms and Ag^{I} centres and through nonclassical $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds.

Comment

The construction of coordination polymers and supramolecular compounds based on multitopic ligands and metal centres represents one of the most rapidly developing fields in current coordination chemistry, owing to their potential as functional materials (Blake *et al.*, 1999, 2000; Kitagawa *et al.*, 2004). In the past few years, supramolecular self-assembly chemistry has developed to allow the rational design and preparation of supramolecular architectures through non-covalent interactions, in which it is crucial to meet both geometric and energetic prerequisites (Pedireddi *et al.*, 1996). The hydrogen bond is undoubtedly the most familiar secondary force in supramolecular assemblies, due to its moderately directional intermolecular interaction which may control molecular packing (Zartilas *et al.*, 2007), and many

studies have focused on it (Lough *et al.*, 2000; Massoud & Langer, 2009). Compared with hydrogen bonds, π - π and metal-metal interactions have been somewhat less studied, and only limited examples generated by a combination of multi-supramolecular interactions have been reported (Goodgame *et al.*, 2002). The naphthalene-1,5-disulfonate anion (nds^{2-}), which possesses six O atoms, has been employed either as a ligand, with multiple binding sites available to construct coordination polymers with varying dimensionalities (Cai, 2004; Lian *et al.*, 2007), or as a counter-ion, forming extensive hydrogen-bonding interactions with other species (Sakwa & Wheeler, 2003; Voogt & Blanch, 2005). Recently, we have pursued systematic investigations into the assembly of Ag^{I} cations with different angular and linear bipodal N-donor ligands, such as rigid aminopyrimidine (Luo, Huang, Zhang *et al.*, 2008; Luo, Huang, Chen *et al.*, 2008; Luo *et al.*, 2009, 2010) and flexible 1,3-bis(4-pyridyl)propane (bpp) or 1,2-bis(4-pyridyl)ethane (bpe) (Luo, Xiong, Dai, 2011; Luo, Xiong, Sun *et al.*, 2011; Xiong *et al.*, 2011), with the principal aim of obtaining supramolecular frameworks or multifunctional coordination polymers. In an attempt to exploit the Ag -disulfonate-bpp system, we successfully obtained the title compound, *catena*-poly[[silver(I)- μ -1,3-bis(4-pyridyl)propane] hemi(naphthalene-1,5-disulfonate) dihydrate], (I), by the solution-phase ultrasonic synthesis technique, and report its crystal structure here.



Compound (I) crystallizes in the monoclinic space group $P2_1/n$ with an asymmetric unit comprising an Ag^{I} cation, one half of an nds^{2-} anion situated on a centre of inversion, a bpp ligand and two solvent water molecules (Fig. 1). The Ag^{I} centre is linearly coordinated by two symmetry-independent N atoms from two bpp ligands [$\text{Ag1}-\text{N1} = 2.1250(19)$ Å, $\text{Ag1}-\text{N2}^{\text{i}} = 2.1353(19)$ Å and $\text{N1}-\text{Ag1}-\text{N2}^{\text{i}} = 171.16(7)^\circ$; symmetry code: (i) $x - \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$]. The average $\text{Ag}-\text{N}$ distance is comparable with those in previously reported Ag -

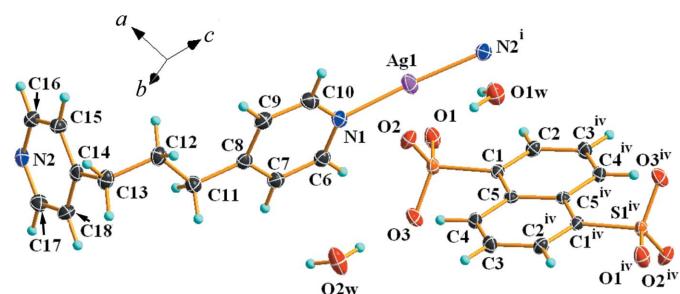
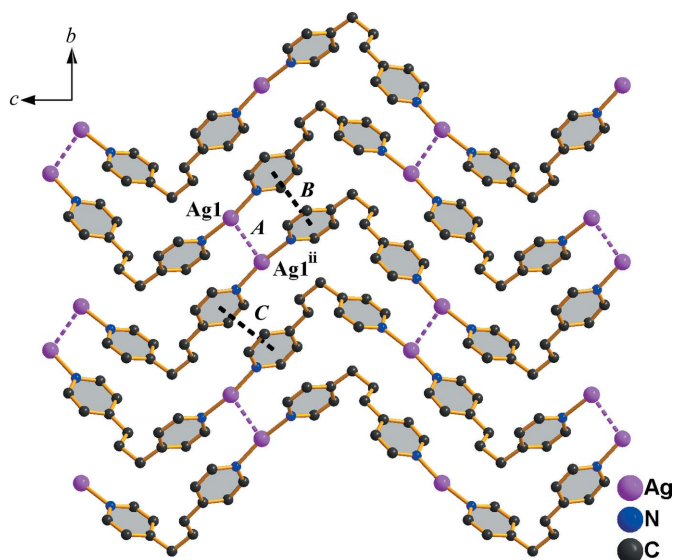


Figure 1

The molecular structure and atom-labelling scheme of (I), showing the coordination environment of the Ag^{I} centre. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (iv) $-x, -y + 1, -z + 1$.]

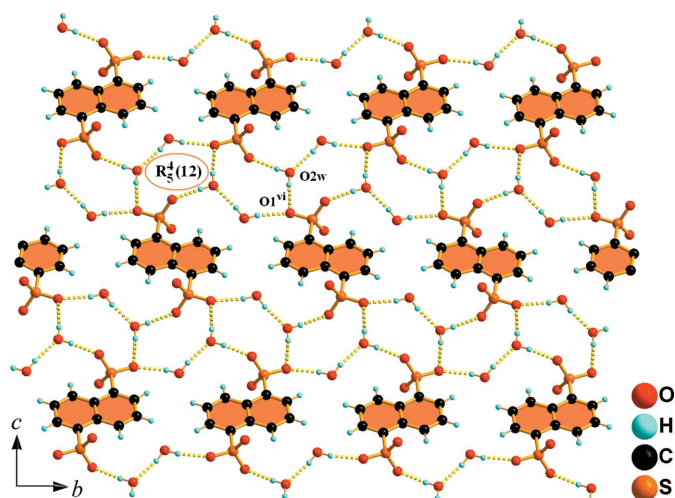

Figure 2

A view of the two-dimensional undulating cationic $[\text{Ag}(\text{bpp})]^+_n$ layer, with the interchain $\text{Ag}\cdots\text{Ag}$ [$A = 3.0718(6) \text{ \AA}$] and $\pi\text{-}\pi$ interactions [$B = 3.6099(6) \text{ \AA}$ and $C = 3.8345(6) \text{ \AA}$] shown as dashed lines. [Symmetry code: (ii) $-x + 1, -y + 1, -z + 1$.]

based compounds (Hao *et al.*, 2009; Steel & Fitchett, 2008) where the Ag^{I} cations have similar coordination geometries.

Generally, the flexible pyridyl-containing bpp ligand can assume four different conformations (TT 9.1–10.1 \AA , TG 8.6–9.2 \AA , GG 6.7–8.6 \AA and GG 3.9 \AA , where $T = \textit{trans}$ and $G = \textit{gauche}$, and the expected ranges in $\text{N}\cdots\text{N}$ separations are given) with respect to the relative orientations of the methylene groups (Carlucci *et al.*, 2002). In (I), each bpp ligand adopts a TG conformation with an $\text{N}\cdots\text{N}$ separation of 8.678(2) \AA and bridges two different metal centres, yielding one-dimensional sinusoidal cationic chains with $\text{Ag}(\text{bpp})$ repeat units [period = 23.439(6) \AA]. Adjacent one-dimensional cationic chains interact with each other through $\text{Ag}\cdots\text{Ag}$ interactions to generate a two-dimensional cationic undulating brick-wall layer of composition $\{[\text{Ag}(\text{bpp})]^+\}_n$ approximately in the bc plane (Fig. 2). The $\text{Ag}\cdots\text{Ag}$ separation of 3.0718(6) \AA in (I) is notably shorter than the sum of the van der Waals radii of two Ag^+ ions (3.44 \AA ; Bondi, 1964), indicating the presence of argentophilic interactions (Pyykkö, 1997).

Among the known structures containing the flexible bpp ligand, similar undulating chains have been found in $[\text{Ag}(\text{bpp})]\text{CF}_3\text{SO}_3\cdot\text{EtOH}$ and $[\text{Ag}(\text{bpp})]\text{NO}_3$ (Carlucci *et al.*, 1997; Bateen *et al.*, 1999), but no metal–metal interactions are found in these compounds, in which the shortest $\text{Ag}\cdots\text{Ag}$ separations are 4.664(1) \AA in the former and 5.287(2) \AA in the latter. The structure of $[\text{Ag}(\text{bpp})]\text{PF}_6$ is similar to (I) in that the $\text{Ag}\cdots\text{Ag}$ contact is 3.0852(9) \AA , but the bpp ligand in $[\text{Ag}(\text{bpp})]\text{PF}_6$ assumes a TT conformation with an $\text{N}\cdots\text{N}$ separation of 9.699(7) \AA (Pan *et al.*, 2001). Besides argentophilic interactions, aromatic $\pi\text{-}\pi$ stacking interactions, with centroid–centroid distances ranging from 3.6099(6) to 3.8345(6) \AA between the pyridyl rings of neighbouring bpp ligands, also exist between the chains in (I), helping to


Figure 3

A view of the two-dimensional water–nds anionic sheet, $\{[(\text{nds})\cdot 2\text{H}_2\text{O}]^{2-}\}_n$, constructed by double anion chains linked by hydrogen bonds (dotted lines). [Symmetry code: (vi) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.]

consolidate the resulting two-dimensional layer. Topologically, if we define the bpp ligands as single spacers connecting the silver(I) centres, this type of layer can be classified as an example of a (6,3) net.

The H_2nds molecule is completely deprotonated to generate the nds^{2-} anion during the synthesis reaction. Each nds^{2-} anion is positioned on an inversion centre and serves as a counter-anion to balance the polymeric host charge, while not participating in the primary coordination of any Ag^{I} centres, reflecting the fact that the coordination ability of bpp is stronger than that of the nds^{2-} anion in this case. Water dimers composed of molecules O1W and O2W interact with the nds^{2-} sulfonate groups *via* strong intermolecular $\text{O}\cdots\text{H}\cdots\text{O}$ hydrogen bonds (Table 1), giving rise to anionic double chains that are interconnected by $\text{O2W}\cdots\text{H2WA}\cdots\text{O1}^{\text{vi}}$ [symmetry code: (vi) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$] hydrogen bonds to form an ordered two-dimensional water–nds anionic layer, $\{[(\text{nds})\cdot 2\text{H}_2\text{O}]^{2-}\}_n$ (Fig. 3) parallel to the cationic $\{[\text{Ag}(\text{bpp})]^+\}_n$ sheet. The hydrogen-bond motif $R_5^4(12)$ (Bernstein *et al.*, 1995), constructed through water molecules and nds^{2-} sulfonate groups, can be found between the double chains.

The two-dimensional cationic and anionic layers in (I) are stacked following an alternating $\dots\text{ABAB}\dots$ sequence, resulting in a three-dimensional metallo-supramolecular sandwich lamellar network, in which the water–anion layered species occupy the interlayer spaces between the metallo-organic networks (Fig. 4). Weak interactions between the sulfonate O atom and the Ag^{I} centre and nonclassical $\text{C}\cdots\text{H}\cdots\text{O}$ hydrogen bonds [$\text{C}\cdots\text{O}$ distances = 3.3443(5)–3.4872(5) \AA] are present in the three-dimensional supramolecular framework. Compared with normal $\text{Ag}\text{-O}$ coordination bonds in silver sulfonates spanning the range 2.3–2.7 \AA (Côté & Shimizu, 2003; Cai, 2004; Gao *et al.*, 2005; Lian *et al.*, 2007), the present $\text{Ag1}\cdots\text{O2}^{\text{ii}}$ interactions of 2.7923(6) \AA [symmetry code: (ii) $-x + 1, -y + 1, -z + 1$] are a

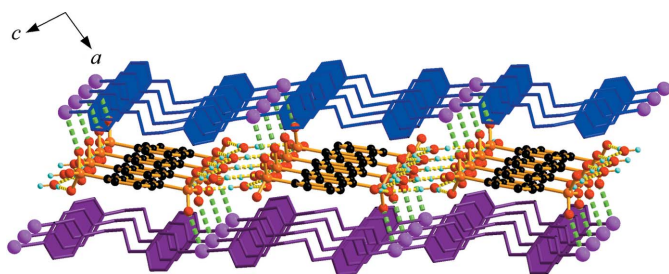


Figure 4
The three-dimensional metallo-supramolecular sandwich-like network of (I) constructed from two-dimensional $\{[\text{Ag}(\text{bpp})]^+\}_n$ and $\{[(\text{nds})\text{-}2\text{H}_2\text{O}]^{2-}\}_n$ layers through $\text{Ag}\cdots\text{O}$ interactions (thick dashed lines).

little longer but still fall in the secondary bonding range (the sum of the van der Waals radii of Ag and O is 3.24 Å; Bondi, 1964). Previously reported $\text{Ag}(\text{bpp})$ salts with simple inorganic anions (such as PF_6^- , ClO_4^- , NO_3^- , etc.) do not exhibit these alternating cation–anion layers. Other $\text{Ag}(\text{bpp})$ salts containing noncoordinated organic carboxylates as counteranions (such as succinate) display similar ...*ABAB*... stacking of cationic and anionic sheets (Luo, Xiong, Sun *et al.*, 2011), but the main difference is that the layers are primarily linked by $\text{O}\cdots\text{H}\cdots\text{O}$ hydrogen bonds between water molecules coordinated to the Ag^{I} cations and the carboxylate groups, instead of by long interlayer $\text{Ag}\cdots\text{O}$ interactions such as those found in (I).

Experimental

A mixture of Ag_2O (115 mg, 0.5 mmol), 1,3-bis(4-pyridyl)propane (205 mg, 1 mmol) and naphthalene-1,5-disulfonic acid (280 mg, 1 mmol) in $\text{CH}_3\text{OH}\text{-H}_2\text{O}$ (10 ml, 1:4 v/v) was subjected to ultrasonic treatment at ambient temperature for 10 min. Aqueous NH_3 (25%) was then added dropwise to the mixture to give a clear solution. This solution was protected from light and concentrated by evaporation at room temperature. Colourless crystals of (I) were isolated after 6 d (yield 45% based on Ag_2O). Analysis calculated for $\text{C}_{18}\text{H}_{21}\text{AgN}_2\text{O}_5\text{S}$: C 44.55, H 4.36, N 5.77%; found: C 44.36, H 4.41, N 5.81%.

Crystal data

$[\text{Ag}(\text{C}_{13}\text{H}_{14}\text{N}_2)](\text{C}_{10}\text{H}_6\text{O}_6\text{S}_2)_{0.5}\cdot 2\text{H}_2\text{O}$	$\beta = 99.55$ (3)°
$M_r = 485.30$	$V = 1867.4$ (6) Å ³
Monoclinic, $P2_1/n$	$Z = 4$
$a = 10.640$ (2) Å	Mo $K\alpha$ radiation
$b = 9.2720$ (19) Å	$\mu = 1.22$ mm ⁻¹
$c = 19.194$ (4) Å	$T = 173$ K
	$0.19 \times 0.16 \times 0.09$ mm

Data collection

Oxford Gemini S Ultra diffractometer	13094 measured reflections
Absorption correction: multi-scan (<i>CrysAlis RED</i> ; Oxford Diffraction, 2008)	3666 independent reflections
$T_{\min} = 0.801$, $T_{\max} = 0.898$	3398 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.036$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$	245 parameters
$wR(F^2) = 0.068$	H-atom parameters constrained
$S = 1.07$	$\Delta\rho_{\text{max}} = 0.55$ e Å ⁻³
3666 reflections	$\Delta\rho_{\text{min}} = -0.94$ e Å ⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D\text{-H}\cdots A$	$D\text{-H}$	$\text{H}\cdots A$	$D\cdots A$	$D\text{-H}\cdots A$
$\text{O1W}\text{-H1WA}\cdots\text{O1}$	0.85	2.04	2.882 (2)	171
$\text{O1W}\text{-H1WB}\cdots\text{O2W}^{\text{vi}}$	0.85	1.95	2.790 (2)	171
$\text{O2W}\text{-H2WA}\cdots\text{O1}^{\text{vi}}$	0.85	2.03	2.874 (2)	174
$\text{O2W}\text{-H2WB}\cdots\text{O3}$	0.85	1.94	2.782 (2)	174
$\text{C6}\text{-H6A}\cdots\text{O2}$	0.95	2.58	3.344 (3)	138
$\text{C7}\text{-H7A}\cdots\text{O3}^{\text{vi}}$	0.95	2.59	3.487 (3)	158

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

All water H atoms were positioned from difference Fourier maps and included as riding atoms, with $\text{O}\text{-H} = 0.85$ Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$. C-bound H atoms were placed in calculated riding positions, with $\text{C}\text{-H} = 0.95$ (aromatic) or 0.99 Å (methylene) and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 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: SQ3295). Services for accessing these data are described at the back of the journal.

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