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Self-assembly of new three-dimensional molecular architectures constructed from silver(I)–hexamethylenetetramine layers with supramolecular interactions

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Three new co-ordination polymers [Ag(μ_3-hmt)](abs) **1**, [Ag(μ_3-hmt)](ns)·0.5(benzene)·2H_2O **2**, and [Ag(μ_3-hmt)]$_2$-[Ag(NH_3)$_2$]$_2$(pma)·3H_2O **3** (hmt = hexamethylenetetramine, abs = 4-aminobenzenesulfonate, ns = 2-naphthalenesulfonate and pma = 1,2,4,5-benzenetetracarboxylate), have been prepared and structurally characterised. In these compounds, the metal ions and the μ_3-hmt ligands are covalently interconnected into hexagonal two-dimensional layers, whereas supramolecular interactions, such as weak Ag ··· O contacts, hydrogen bonds and/or π–π stacking, play an important role in the construction of three-dimensional molecular architectures. The observation of dimeric [Ag(NH_3)$_2$]$_2^{2+}$ species trapped in such co-ordination surroundings in **3** is unprecedented.

Introduction

Over the last decade attention has focused on the use of supramolecular interactions (such as hydrogen bonding, π–π interactions, *etc.*), and also co-ordinate covalent bonds, in the controlled assembly of supramolecular architectures.[1,2] Supramolecular interactions may play a dominant role in crystal engineering because they combine strength (a prerequisite of stability) with directionality (a prerequisite of reproducibility).[2–4] On the other hand, the combination of hexamethylenetetramine (hmt) as a polydentate ligand and silver(I) can produce a wide variety of supramolecular architectures.[5–11] We have recently exploited stable hexagonal two-dimensional layers to construct three-dimensional architectures *via* either intercalation of the lateral aromatic ligands or bridging of linear dicarboxylate as molecular pillars, featuring small channels.[10] As a sequel to our systematic investigation on Ag–hmt supramolecular architectures, we now report here the results of an attempt to construct co-ordination polymers, namely [Ag(μ_3-hmt)](abs) **1**, [Ag(μ_3-hmt)](ns)·0.5(benzene)·2H_2O **2**, and [Ag(μ_3-hmt)]$_2$[Ag(NH_3)$_2$]$_2$(pma)·3H_2O **3** (hmt = hexamethylenetetramine, abs = 4-aminobenzenesulfonate, ns = 2-naphthalenesulfonate and pma = 1,2,4,5-benzenetetracarboxylate), in which the metal ions and μ_3-hmt ligands are also connected into hexagonal two-dimensional layers. Different from the previously reported Ag–hmt complexes,[10,11] the supramolecular interactions, such as weak Ag ··· O contacts, hydrogen bonds and/or π–π stacking, are observed here, playing a very important role in the construction of three-dimensional molecular architectures. The observation of dimeric [Ag(NH_3)$_2$]$_2^{2+}$ species trapped in such co-ordination surroundings as found in **3** is unprecedented.

Experimental

Materials

The compounds Ag(abs), Ag(ns) and Ag$_4$(pma) were prepared according to the literature methods.[12] The reagents and solvents employed were commercially available and used as received without further purification. The C, H, N microanalyses were carried out with a Perkin-Elmer 240 elemental analyser. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Nicolet 5DX spectrometer.

Synthesis

[Ag(μ_3-hmt)](abs) 1. A solution (5 cm^3) of hmt (0.140 g, 1.0 mmol) was added dropwise to a stirred MeCN solution (5 cm^3) of Ag(abs) (0.264 g, 1.0 mmol) at 50 °C for 30 min. The resulting yellow solution was allowed to stand in air at room temperature for two weeks, yielding pale yellow crystals in good yield (72%). Anal. calc. for $C_{12}H_{18}AgN_5O_3S$ **1**: C, 34.30; H, 4.32; N, 16.67; S, 7.63. Found: C, 34.22; H, 4.36; N, 16.71; S, 7.68%. IR (KBr, cm^{-1}): 3490m, 3427s, 3551s, 3248m, 3034w, 2956m, 2881w, 1652s, 1604s, 1505m, 1456m, 1387w, 1320m, 1297w, 1238s, 1173vs, 1123s, 1030s, 1006vs, 943m, 917m, 819s, 799s, 778m, 695vs, 656m, 580s, 556s, 505m.

[Ag(μ_3-hmt)](ns)·0.5(benzene)·2H_2O 2. A solution (5 cm^3) of hmt (0.140 g, 1.0 mmol) in EtOH was added dropwise to a stirred benzene solution (5 cm^3) of Ag(ns) (0.315 g, 1.0 mmol) at 50 °C for 30 min. The mixture was dissolved by the dropwise addition of aqueous NH_3 solution. The resulting pale yellow solution was allowed to stand in air at room temperature for two weeks, yielding pale yellow crystals (yield *ca.* 58%). Anal. calc. for $C_{19}H_{26}AgN_4O_5S$ **2**: C, 43.03; H, 4.94; N, 10.56; S, 6.05. Found: C, 43.24; H, 5.01; N, 10.67; S, 6.01%. IR (KBr, cm^{-1}): 3454s (br), 3054w, 2956m, 2886w, 1667w, 1637m, 1592w, 1501w, 1460m, 1385m, 1347w, 1272m, 1238vs, 1190vs, 1092s, 1008vs, 921m, 870w, 805s, 759m, 680s, 623m, 565s, 508m, 477m, 420w.

[Ag(μ_3-hmt)]$_2$[Ag(NH_3)$_2$]$_2$(pma)·3H_2O 3. A solution (5 cm^3) of hmt (0.140 g, 1.0 mmol) was added dropwise to a stirred EtOH solution (5 cm^3) of Ag$_4$(pma) (0.340 g, 0.5 mmol) at 50 °C for 30 min. The mixture was dissolved by the dropwise addition of aqueous NH_3 solution. The resulting colourless solution was allowed to stand in air at room temperature for two weeks, yielding colourless crystals (yield *ca.* 52%). Anal. calc. for $C_{22}H_{44}Ag_4N_{12}O_{11}$ **3**: C, 24.37; H, 4.09; N, 15.50.

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Table 1 Crystal data for complexes **1**–**3**

	1	**2**	**3**
Formula	$C_{12}H_{18}AgN_5O_3S$	$C_{19}H_{26}AgN_4O_5S$	$C_{22}H_{44}Ag_4N_{12}O_{11}$
M	420.24	530.37	1084.17
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$Pmn2_1$ (no. 31)	$Pna2_1$ (no. 33)	*Pnnm* (no. 58)
a/Å	6.562(5)	30.32(2)	10.588(4)
b/Å	13.342(8)	10.923(10)	23.73(1)
c/Å	8.555(3)	6.349(3)	6.374(1)
V/Å^3	749.0(8)	2103(3)	1601.4(10)
Z	2	4	2
D_c/g cm^{-3}	1.863	1.675	2.248
μ(Mo-Kα)/mm^{-1}	1.505	1.097	2.487
No. unique data	2251	2095	1999
No. data with $I \geq 2\sigma(I)$	1148	2018	1906
R_1 [$I \geq 2\sigma(I)$]	0.0254	0.0479	0.0499
wR_2 (all data)	0.0645	0.1316	0.1424

Found: C, 24.42; H, 3.94; N, 15.46%. IR (KBr, cm^{-1}): 3436s, 3259m (br), 2952m, 2880m, 1607 m, 1567vs, 1487m, 1460m, 1417s, 1372vs, 1323m, 1236s, 1137w, 1052w, 1008vs, 920w, 864w, 812m, 691m, 666m, 604m, 544m, 512m, 460w.

X-Ray crystallography

Diffraction intensities for the three complexes were collected at 21 °C on a Siemens R3m diffractometer using the ω-scan technique. Lorentz-polarization and absorption corrections were applied.[13] The structures were solved with direct methods and refined with full-matrix least-squares techniques using the SHELXS-97 and SHELXL-97 programs, respectively.[14,15] Anisotropic thermal parameters were applied to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically (C–H 0.96 Å and N–H 0.90 Å); the aqua hydrogen atoms were located from difference maps and refined with isotropic temperature factors. The hemi-solvate benzene molecule in **2** and lattice water molecules in **3** are disordered and were refined with 1/2 site occupancies each with geometric restraints. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[16] The absolute structure parameter was refined to −0.02(4) for **1** and to 0.1(1) for **2**.[17] Crystal data as well as details of data collection and refinement for the complexes are summarised in Table 1. Selected bond distances and bond angles are listed in the Table 2. Drawings were produced with SHELXTL.[18]

CCDC reference numbers 169729–169731.

See http://www.rsc.org/suppdata/dt/b1/b106925j/ for crystallographic data in CIF or other electronic format.

Results

Crystal structures

The structure of **1** consists of two-dimensional infinite wavy cationic co-ordination layers of hexagonal units in a boat-type conformation (Fig. 1a), which are highly similar to those in [Ag(μ_3-hmt)]X (X = ClO_4^- or $S_2O_6^{2-}$).[5,8] Each hexagonal unit comprises three Ag(I) atoms and three hmt ligands each at a corner, in which the Ag(I) atoms are co-ordinated in a trigonal geometry to three nitrogen atoms [Ag(1)–N 2.373(4) and 2.433(4) Å, N–Ag(1)–N 109.7(1) and 119.0(2)°] from different hmt ligands. As shown in Fig. 1b, the counter ions, uncoordinated abs anions, are alternatively slanted up and down and are located between the hexagonal two-dimensional layers with weak Ag ··· O contacts [Ag(1) ··· O(2) 2.770(8) Å, well beyond the values (2.38–2.62 Å) reported for the sulfonate silver(I) complexes[19]] and C–H ··· O hydrogen bonds[20] [C(16) ··· O(1) 3.416 Å] between the abs oxygen atoms and hmt carbon atoms, resulting in a three-dimensional molecular architecture. As shown in Fig. 1c, each abs amino nitrogen atom forms two donor hydrogen bonds with two oxygen atoms of sulfonic groups from different abs anions [N(1) ··· O(2) 2.953(6) Å], resulting in zipper-like hydrogen-bonded layers.

The structure of **2** is similar to that of **1**, featuring hexagonal two-dimensional layers. The Ag(I) atom in **2** is also co-ordinated in a trigonal geometry by three nitrogen atoms [Ag(1)–N 2.389(7)–2.42(1) Å; N–Ag(1)–N 106.8(2)–127.3(4)°] from different hmt ligands. As shown in Fig. 2a, the uncoordinated ns anions are alternatively orientated vertically up and down the layers in pairs, and the lattice water molecules, pillar the two-dimensional Ag–hmt layers with weak Ag ··· O contacts [Ag(1) ··· O(1) 2.73(1) Å and Ag(1) ··· O(1w) 2.70(1) Å] and C–H ··· O hydrogen bonds [C(16) ··· O(1) 3.321 Å; while C(12) ··· O(2w) 3.403 Å] between the ns oxygen atoms and hmt carbon atoms. Hydrogen-bonding between these interlayer molecules was observed, as evidenced by the O ··· O distances of 2.84(3) and 2.95(2) Å. It should be noted that the supramolecular structure is further stabilised by the aromatic π–π stacking interactions. As shown in Fig. 2, the solvate benzene molecules are clathrated between adjacent pairs of ns anions, and the adjacent aromatic rings are separated at a face-to-face distance of 3.49 or 3.40 Å, and are arranged in an offset fashion, suggesting the presence of π–π stacking interactions.

As shown in Fig. 3a, the structure of **3** also consists of hexagonal two-dimensional layers, and the Ag(I) atom in the hexagonal units is also in a trigonal geometry co-ordinated by three nitrogen atoms [Ag(1)–N 2.381(6)–2.403(4) Å, N–Ag(1)–N 108.6(2)–120.5(1)°] from different hmt ligands. Similar to those in both **1** and **2**, the uncoordinated pma anions are orderly located between the layers with weak Ag ··· O contacts [Ag(1) ··· O(3) 2.645(6) Å] and C–H ··· O hydrogen bonds [C ··· O 3.321–3.468 Å] between the carboxy oxygen atoms and hmt carbon atoms. It should be pointed out that there is another crystallographically independent Ag(2) atom, which is co-ordinated in a virtually linear geometry by two ammonia ligands [Ag(2)–N 2.104(10) and 2.135(8) Å, N–Ag(1)–N 177.0(4)°]. The most significant structural feature presented here is that a pair of two bridged Ag(2) atoms are only separated by 3.211(2) Å (Fig. 3b), indicating a relatively weak Ag ··· Ag interaction,[8,9,21] which results in a unique dimeric $[Ag(NH_3)_2]_2^{2+}$ species. To the best of our knowledge, no dimeric $[Ag(NH_3)_2]_2^{2+}$ species has been reported so far; in contrast, monomeric $[Ag(NH_3)_2]^+$ cations have been observed in the complexes $[Ag(NH_3)_2]X$ (X = SO_4^{2-}, NO_3^-, BH_4^-).[22] Although the dimeric $[Ag(NH_3)_2]_2^{2+}$ species are clathrated between the adjacent pma anions (Fig. 3a), no metal–π interaction has been observed since the closest Ag ··· C contact (3.34 Å) is well beyond the values reported for silver(I) complexes of other polycyclic aromatic compounds.[23] However, the ammonia ligands form donor hydrogen bonds with the carboxylate oxygen atoms of adjacent pma anions [N(4) ··· O(3) 2.923(8) Å]. Moreover, hydrogen bonds between the ammonia

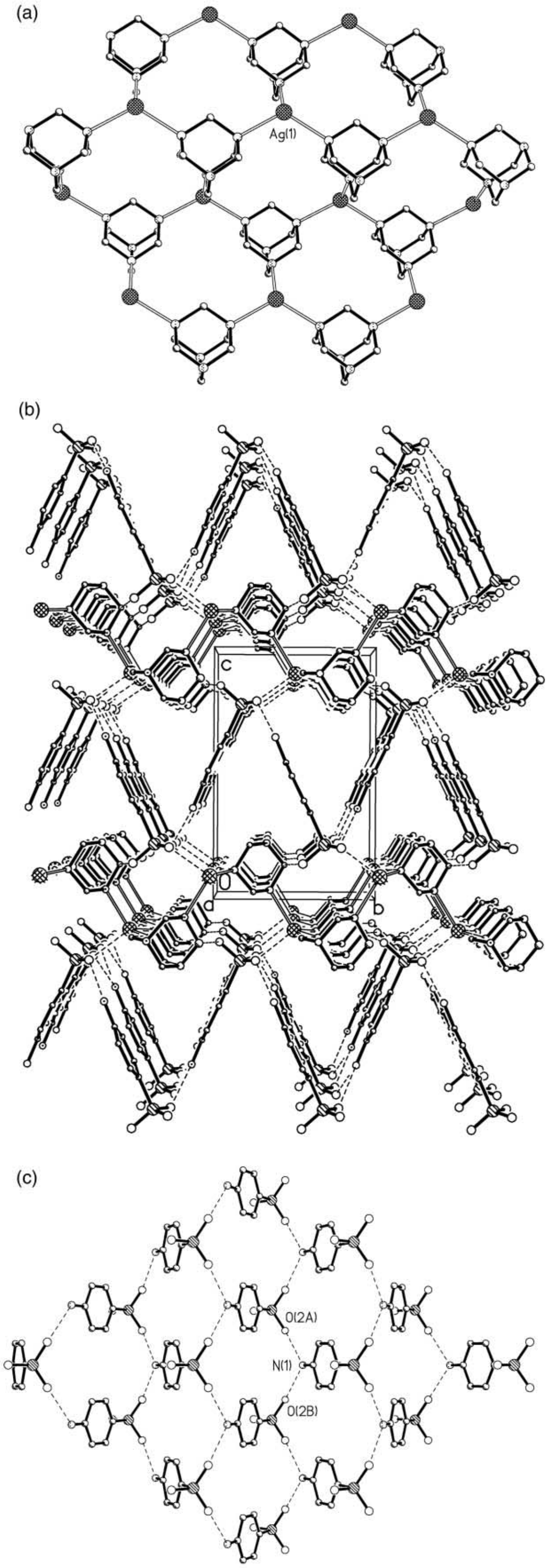

Fig. 1 Perspective views of the layer viewed along the *a*-axis (a), the three-dimensional molecular architecture viewed along the *a*-axis (b), and the zipper-like hydrogen-bonded layer viewed along the *c*-axis (c) in **1**.

ligands and lattice water molecules are also observed [N(5) ··· O(2Wb) 3.26(3) Å]. Such supramolecular interactions may be responsible here for the stabilisation of the $[Ag(NH_3)_2]_2^{2+}$ species.

Table 2 Selected bond lengths (Å) and angles (°) for complexes **1**–**3**

Complex **1**			
Ag(1)–N(2a)	2.373(4)	Ag(1) ··· O(2)	2.770(8)
Ag(1)–N(2b)	2.373(4)	N(1) ··· O(2c)	2.953(6)
Ag(1)–N(4)	2.433(4)		
N(2a)–Ag(1)–N(2b)	119.0(2)	N(2b)–Ag(1)–N(4)	109.7(1)
N(2a)–Ag(1)–N(4)	109.7(1)		
Complex **2**			
Ag(1)–N(2a)	2.389(7)	O(1W) ··· O(3c)	2.84(3)
Ag(1)–N(1)	2.40(1)	O(1W) ··· O(2a)	2.95(2)
Ag(1)–N(3b)	2.42(1)	O(2W) ··· O(2b)	2.86(2)
Ag(1) ··· O(1)	2.73(1)	O(1) ··· O(2w)	2.91(2)
Ag(1) ··· O(1w)	2.70(1)		
N(2a)–Ag(1)–N(1)	127.3(4)	N(1)–Ag(1)–N(3b)	106.8(2)
N(2a)–Ag(1)–N(3b)	125.3(4)		
Complex **3**			
Ag(1)–N(3a)	2.381(6)	N(4) ··· O(3d)	2.923(8)
Ag(1)–N(1)	2.403(4)	N(4) ··· O(3e)	2.923(8)
Ag(1)–N(1b)	2.403(4)	N(5) ··· O(3f)	3.107(9)
Ag(2)–N(4)	2.135(8)	N(5) ··· O(3g)	3.107(9)
Ag(2)–N(5)	2.104(10)	N(5) ··· O(2Wb)	3.26(3)
Ag(1) ··· O(3)	2.645(6)	O(2W) ··· O(2Wh)	2.81(6)
Ag(2) ··· Ag(2c)	3.211(2)		
N(3a)–Ag(1)–N(1)	120.5(1)	N(1)–Ag(1)–N(1b)	108.6(2)
N(3a)–Ag(1)–N(1b)	120.5(1)	N(5)–Ag(2)–N(4)	177.0(4)

Symmetry codes: a) $x + 1/2, -y + 2, z + 1/2$; b) $-x + 3/2, -y + 2, z + 1/2$; c) $-x + 3/2, -y + 1, z - 1/2$ for **1**; a) $-x + 1/2, y - 1/2, z + 1/2$; b) $x, y, z + 1$; c) $-x + 1/2, y - 1/2, z - 1/2$ for **2**; a) $x + 1/2, -y + 1/2, z + 1/2$; b) $x, y, -z$; c) $-x + 1, -y + 1, -z$; d) $x - 1/2, -y + 1/2, z - 1/2$; e) $x - 1/2, -y + 1/2, -z + 1/2$; f) $-x + 3/2, y + 1/2, -z + 1/2$; g) $-x + 3/2, y + 1/2, z - 1/2$; h) $-x + 2, -y + 1, -z - 1$ for **3**.

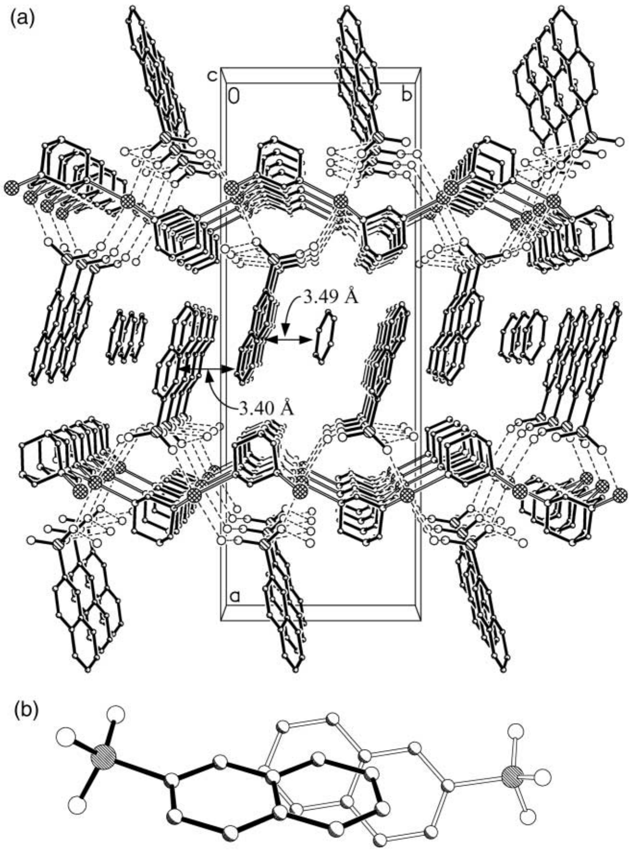

Fig. 2 Perspective view of the π–π stacking interactions between ns and benzene solvate (a) and π–π stacking interactions of ns (b) in **2**. The C–H ··· O hydrogen bonds are omitted for clarity.

Discussion

We and others have previously reported many kinds of Ag–hmt supramolecular architectures, in which the counter ions

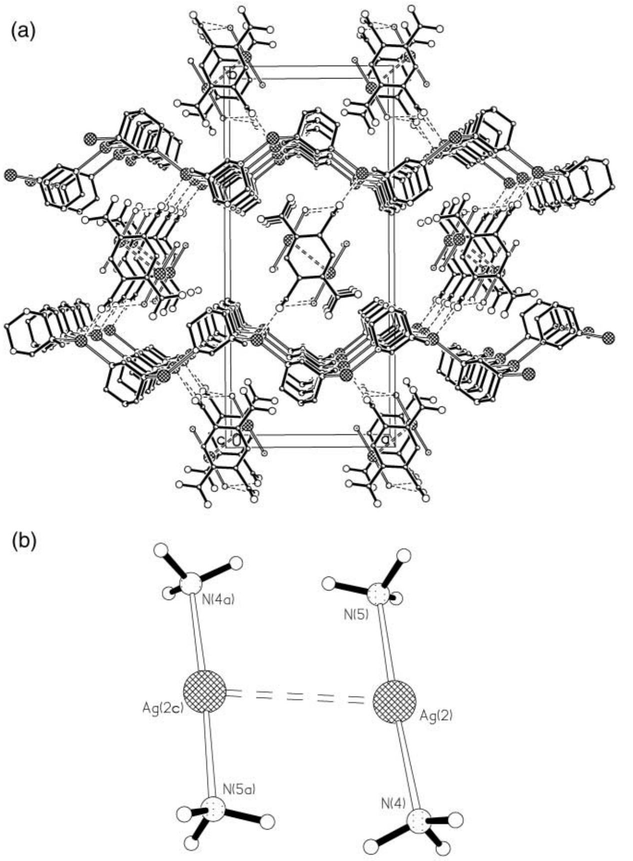

Fig. 3 Perspective views of the three-dimensional molecular architecture viewed along the *c*-axis (a) and the dimeric $[Ag(NH_3)_2]_2^{2+}$ species (b) in **3**. The lattice water molecules and the C–H · · · O hydrogen bonds are omitted for clarity.

range from small anions to aromatic monocarboxylates and linear dicarboxylates, and more than half of them consist of stable hexagonal two-dimensional [Ag(μ$_3$-hmt)] layers. To our knowledge, although the Ag(I) atoms can assume co-ordination geometries spanning all situations including linear, trigonal and tetrahedral, a chelate mode of the counter ions in co-ordination to the Ag(I) atoms within the very stable hexagonal two-dimensional layers is highly unlikely due to geometric restriction. This fact has been exploited by us to construct three-dimensional architectures based on stable hexagonal two-dimensional layers *via* either intercalation of the lateral aromatic ligands or bridging of linear dicarboxylate as molecular pillars, featuring small channels.[10] However, sulfonates are of weak ligation ability and usually act in a chelating modes rather than a monodentate one to ligate a Ag(I) atom.[19] Therefore, both the stability of the hexagonal two-dimensional layers and the weak co-ordination ability of sulfonate may exclude any significant co-ordination interaction between the hexagonal two-dimensional layers and the sulfonate groups in both **1** and **2**, where the contacts between the silver(I) and sulfonate oxygen atoms are all larger than 2.70 Å, well beyond those (2.38–2.62 Å) reported for other silver(I) sulfonate complexes, indicating only weak Ag · · · O interactions. Similar to the sulfonate, the pma ligands in **3** connect with the Ag(I) atoms in the layers with weak Ag · · · O contacts.

Since no co-ordination bonds between the counter ions and metal atoms are observed for **1**–**3**, supramolecular interactions, such as weak Ag · · · O contacts, hydrogen bonds and/or π–π stacking, play a very important role in the construction of molecular architectures. It should also be noted that the unique dimeric $[Ag(NH_3)_2]_2^{2+}$ species in **3** are trapped in complicated supramolecular interactions.

We have successfully synthesised three new Ag–hmt complexes, in which supramolecular interactions, such as weak Ag · · · O contacts, hydrogen bonds and/or π–π stacking play an important role in the construction of three-dimensional molecular architectures. This work implies that supramolecular interactions may be used in pillaring co-ordination layers into three-dimensional molecular architectures.

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