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Syntheses and structures of three two-dimensional silver(I)–hexamethylenetetramine co-ordination polymers with new topological motifs

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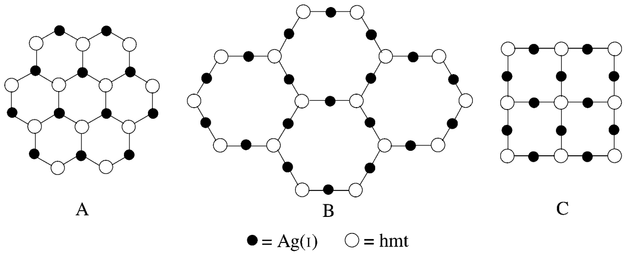
Received 16th February 2001, Accepted 8th May 2001
First published as an Advance Article on the web 11th June 2001

Three new co-ordination complexes, $[Ag(\mu\text{-hmt})(cin)]\cdot 2H_2O$ **1**, $[Ag_2(\mu_3\text{-hmt})(sal)_2]$ **2**, and $[Ag_2(\mu\text{-hmt})(\mu_3\text{-hmt})(ssa)]$ **3** (hmt = hexamethylenetetramine (1,3,5,7-tetraazatricyclo[3.3.1^{3,7}]decane), cin = cinnamate, sal = salicylate and ssa = 5-sulfosalicylate), have been prepared and structurally characterised. All of these complexes contain different new topological motifs of two-dimensional Ag–hmt nets. Among them, **1** has two-dimensional infinite co-ordination layers featuring compressed hexagonal units each consisting of six Ag(I) and four μ-hmt ligands as spacers. **2** has two-dimensional infinite wavy co-ordination layers with decagonal and small hexagonal units; each decagonal unit comprises six Ag(I) and four μ_3-hmt ligands, and each small hexagonal unit comprises four Ag(I) and two μ_3-hmt ligands. **3** has two-dimensional infinite highly undulated Ag–hmt layers with irregular decagonal units each consisting of five Ag(I), two μ-hmt and three μ_3-hmt ligands.

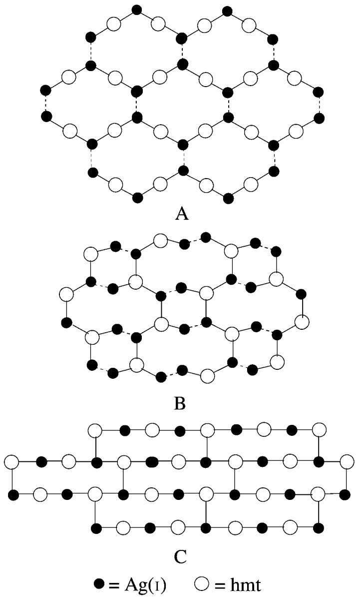
Introduction

Crystal engineering and the design of solid-state architectures of co-ordination polymers are very attractive fields in recent years.[1,2] Assembly of such extended supramolecular architectures by selecting the chemical structure of organic ligands and the co-ordination geometry of metal ions may yield a large number of new networks exhibiting interesting topologies and potential properties as new materials.[3–7] We and others have found that combination of hexamethylenetetramine (1,3,5,7-tetraazatricyclo[3.3.1^{3,7}]decane) (hmt) as a polydentate ligand and silver(I) can produce a wide variety of supramolecular architectures,[5–13] featuring three topological motifs in the two-dimensional Ag–hmt nets as illustrated in Scheme 1.[7,8,11–13] We have used the stable hexagonal two-dimensional nets (Scheme 1(A)) to construct three-dimensional architectures *via* either intercalation of lateral aromatic ligands or bridging of linear dicarboxylate as molecular pillars, which shows small channels (<4 × 11 Å) partly due to the small sizes of the above hexagonal rings.[13] Expansion of the hexagonal rings may be useful for construction of three-dimensional architectures with larger channels. On the other hand, so far the one two-dimensional net with larger hexagonal units (Scheme 1(B)) has been documented in $[Ag_3(\mu_3\text{-hmt})_2(H_2O)_4][PF_6]_3$ recently;[7] no two-dimensional Ag–hmt net consisting of dimeric silver(I) fragments has been reported to date, although hmt–Ag_2L_2–hmt fragments (L = acetate, maleate or benzoate) have been found in three three-dimensional neutral honeycomb-like networks.[11]



Scheme 1 Three known topological motifs of two-dimensional Ag–hmt nets: hexagons (A); big hexagons (B); squares (C).

As a sequel to our systematic investigation on Ag–hmt co-ordination networks, we now report here three new co-ordination polymers, namely $[Ag(\mu\text{-hmt})(cin)]\cdot 2H_2O$ **1**, $[Ag_2(\mu_3\text{-hmt})(sal)_2]$ **2**, and $[Ag_2(\mu\text{-hmt})(\mu_3\text{-hmt})(ssa)]$ **3** (cin = cinnamate, sal = salicylate, ssa = 5-sulfosalicylate), which contain different new topological motifs in two-dimensional Ag–hmt nets as illustrated in Scheme 2. Among them, **1** has two-dimensional infinite co-ordination layers with distorted hexagonal units, **2** two-dimensional infinite wavy co-ordination layers with decagonal and small hexagonal units, while **3** has two-dimensional



Scheme 2 Three new topological motifs of two-dimensional Ag–hmt nets reported in this work: compressed hexagons (A); decagons and small hexagons (B); decagons (symbolised as rectangles) (C).

DOI: 10.1039/b101539g

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infinite highly undulated neutral layers with irregular decagonal units. The two-dimensional nets in **1** and **2** are the first examples constructed by dimeric silver(I) fragments in two-dimensional Ag–hmt nets.

Experimental

Materials

The compounds $Ag_2(cin)_2$, $Ag_2(sal)_2$ and $Ag_2(ssa)$ were prepared according to the literature method.[14] 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-hmt)(cin)]·2H$_2$O 1. A solution (5 cm^3) of hmt (0.140 g, 1.0 mmol) in CH_2Cl_2 was added dropwise to a stirred MeCN solution (5 cm^3) of $Ag_2(cin)_2$ (0.255 g, 0.5 mmol) at 50 °C for 15 min. The mixture was dissolved by 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 in good yield (84%). Calc. for $C_{15}H_{23}AgN_4O_4$ **1**: C, 41.78; H, 5.38; N, 12.99. Found: C, 41.82; H, 5.46; N, 12.76%. IR (KBr, cm^{-1}): 3444m, br, 3093w, 2952m, 2882w, 1595s, 1553vs, 1453w, 1391s, 1229s, 1173w, 1068w, 1004vs, 835w, 814m, 709s, 681s, 512w, 428w.

[Ag$_2$(μ$_3$-hmt)(sal)$_2$] 2. This was prepared as for **1** (yield *ca.* 68%) except that the molar ratio of Ag : hmt was changed to 1 : 1. Calc. for $C_{20}H_{22}Ag_2N_4O_6$ **2**: C, 38.12; H, 3.52; N, 8.89. Found: C, 38.08; H, 3.48; N, 8.92%. IR (KBr, cm^{-1}): 3422m, br, 3067w, 2953m, 2879m, 2691w, 2611w, 1595vs, 1487s, 1462vs, 1390s, 1339m, 1301m, 1235s, 1143m, 1085w, 1053w, 1005vs, 922w, 860m, 811m, 748m, 696m, 668m, 534w, 509w, 463w.

[Ag$_2$(μ-hmt)(μ$_3$-hmt)(ssa)] 3. A solution (5 cm^3) of hmt (0.140 g, 1.0 mmol) in CH_2Cl_2 was added dropwise to a stirred EtOH solution (5 cm^3) of $Ag_2(ssa)$ (0.216 g, 0.5 mmol) at 50 °C for 15 min. The resulting yellow solution was allowed to stand in air at room temperature for a week, yielding yellow crystals (76%). Calc. for $C_{19}H_{28}Ag_2N_8O_6S$ **3**: C, 32.04; H, 3.96; N, 15.73; S, 4.50. Found: C, 32.08; H, 4.02; N, 15.69; S, 4.48%. IR (KBr, cm^{-1}): 3440m, br, 3061w, 2939m, 2890m, 2692w, 1626s, 1578vs, 1467s, 1437s, 1371m, 1315m, 1287m, 1238vs, 1188vs, 1147s, 1121m, 1067m, 1026vs, 1003vs, 914m, 890w, 830s, 806s, 722m, 669s, 591s, 558w, 510m, 453w.

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.[15] The structures were solved with direct methods and refined with the full-matrix least-squares technique using the SHELXS 97 and SHELXL 97 programs, respectively.[16,17] Anisotropic thermal parameters were applied to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically (C–H 0.96 Å); the aqua hydrogen atoms were located from difference maps and refined with isotropic thermal parameters. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[18] Crystal data as well as details of data collection and refinement for the complexes are summarised in Table 1. Selected bond distances and angles are listed in Table 2. Drawings were produced with SHELXTL.[19]

CCDC reference numbers 159017–159019.

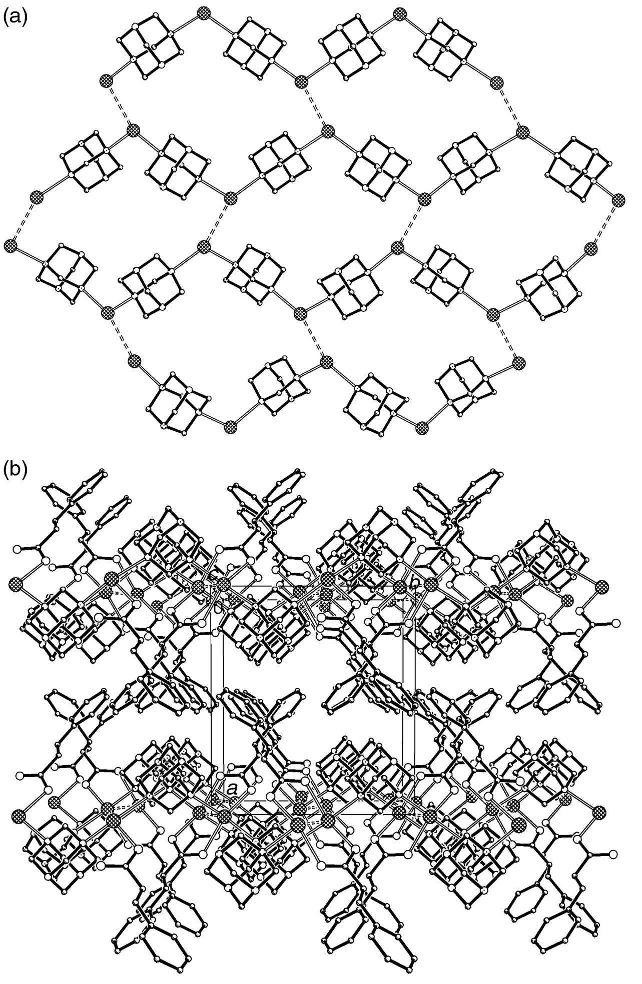

Fig. 1 Perspective views of the layer viewed along the *a* axis (a) and the three-dimensional network viewed along the *c* axis (b) in **1**. The lattice water molecules are omitted for clarity.

See http://www.rsc.org/suppdata/dt/b1/b101539g/ for crystallographic data in CIF or other electronic format.

Results and discussion

Crystal structures

Complexes **1** and **2** consist of different two-dimensional Ag–hmt nets constructed from hmt ligands and dimeric silver(I) fragments, featuring two new topological motifs. In **1** the dimeric Ag_2(μ-cin)$_2$ fragments are bridged by hmt ligands, each using two nitrogen atoms, into infinite chains along the *c*-axis direction, which are similar to those found in [Ag$_2$(μ$_4$-hmt)(μ-O$_2$CMe)][MeCO$_2$]·4.5H$_2$O, [Ag$_2$(μ$_4$-hmt)(μ$_3$-maleate)]·5H$_2$O, [Ag$_3$(μ$_4$-hmt)(μ-O$_2$CPh)$_3$].[11] These chains are further connected by the μ-hmt ligands, resulting in a two-dimensional infinite coordination layer with compressed hexagonal units, as illustrated in Fig. 1(a) and Scheme 2(A). It should be noted that previously hmt was found to play the role of a node in all two-dimensional Ag–hmt nets.[6–8,11–13] Therefore, complex **1** is the first example of two-dimensional Ag–hmt nets with μ-hmt ligands as spacers. Each hexagonal unit is organised by six Ag(I) atoms and four μ-hmt ligands, in which the Ag(I) is joined by two μ-carboxylate bridges of cin [Ag–O 2.289(2) and 2.336(2) Å] with the Ag···Ag distance of 3.120(1) Å, indicating a relatively weak interaction.[20] Similar bis(μ-carboxylate)-bridged dinuclear cores have been reported in a number of silver(I) carboxylates[21] as well as our previous three-dimensional complexes [Ag$_2$(μ$_4$-hmt)(μ-O$_2$CMe)][MeCO$_2$]·4.5H$_2$O and [Ag$_3$(μ$_4$-hmt)(μ-O$_2$CPh)$_3$].[11] Each Ag(I) is further ligated by two nitrogen atoms from two different hmt ligands [Ag–N 2.377(2) and

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

	1	**2**	**3**
Formula	$C_{15}H_{23}AgN_4O_4$	$C_{20}H_{22}Ag_2N_4O_6$	$C_{19}H_{28}Ag_2N_8O_6S$
M	431.24	630.16	712.29
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$ (no. 14)	$C2/c$ (no. 15)	$Pbca$ (no. 61)
a/Å	12.219(3)	24.066(17)	17.059(10)
b/Å	10.842(3)	10.856(7)	11.247(5)
c/Å	13.006(3)	18.750(8)	24.520(8)
β/°	94.140(10)	120.81(1)	
V/Å^3	1718.5(7)	4207(4)	4704(4)
Z	4	8	8
D_c/g cm^{-3}	1.667	1.990	2.011
μ(Mo-Kα)/mm^{-1}	1.200	1.909	1.809
No. unique data	4331	5216	5483
No. data with $I \geq 2\sigma(I)$	4146	5097	5246
$R1$ $[I \geq 2\sigma(I)]$	0.0321	0.0503	0.0543
$wR2$ (all data)	0.0857	0.1328	0.1303

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

Complex **1**			
Ag(1)–O(2)	2.289(2)	Ag(1)–N(1)	2.433(2)
Ag(1)–O(1a)	2.336(2)	Ag(1)–N(2b)	2.377(2)
Ag(1)$\cdots$Ag(1a)	3.120(1)	O(1w)$\cdots$O(2w)	3.032(7)
O(2)$\cdots$O(1w)	2.754(4)	O(2w)$\cdots$N(3c)	3.072(5)
O(2)–Ag(1)–O(1a)	137.47(9)	O(2)–Ag(1)–N(2b)	112.80(8)
O(1a)–Ag(1)–N(2b)	98.53(8)	N(2b)–Ag(1)–N(1)	120.71(7)
O(2)–Ag(1)–N(1)	98.62(8)	O(2)–Ag(1)–Ag(1a)	78.48(6)
O(1a)–Ag(1)–N(1)	88.50(8)		
Complex **2**			
Ag(1)–N(1)	2.426(4)	Ag(2)–N(2a)	2.338(4)
Ag(1)–O(22)	2.262(4)	Ag(2)–N(3b)	2.376(4)
Ag(1)–O(11)	2.316(4)	Ag(2)–O(12)	2.387(4)
Ag(2)–O(21)	2.279(4)	Ag(1)$\cdots$Ag(2)	3.042(1)
O(12)$\cdots$O(13)	2.495(6)	O(22)$\cdots$O(23)	2.527(6)
O(22)–Ag(1)–O(11)	144.6(16)	O(22)–Ag(1)–N(1)	96.4(2)
O(11)–Ag(1)–N(1)	87.4(1)	N(2a)–Ag(2)–O(12)	96.9(2)
O(21)–Ag(2)–N(2a)	103.4(2)	N(3b)–Ag(2)–O(12)	105.8(2)
O(21)–Ag(2)–N(3b)	91.4(2)	N(2a)–Ag(2)–N(3b)	125.8(1)
O(21)–Ag(2)–O(12)	138.1(2)		
Complex **3**			
Ag(1)–N(5)	2.339(5)	Ag(2)–N(3)	2.178(5)
Ag(1)–N(1)	2.365(5)	Ag(2)–N(8b)	2.196(5)
Ag(1)–N(6a)	2.409(5)	Ag(2)–O(6c)	2.493(6)
Ag(1)–O(2)	2.461(6)	O(2)$\cdots$O(3)	2.527(8)
N(5)–Ag(1)–N(1)	111.2(2)	N(6a)–Ag(1)–O(2)	85.7(2)
N(5)–Ag(1)–N(6a)	115.8(2)	N(3)–Ag(2)–N(8b)	169.6(2)
N(1)–Ag(1)–N(6a)	116.0(2)	N(3)–Ag(2)–O(6c)	92.1(2)
N(5)–Ag(1)–O(2)	132.7(2)	N(8b)–Ag(2)–O(6c)	96.2(2)
N(1)–Ag(1)–O(2)	92.8(2)		

Symmetry codes: (a) $-x, -y, -z$; (b) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; (c) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$ for **1**; (a) $x, -y, z + \frac{1}{2}$; (b) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$ for **2**; (a) $-x + \frac{1}{2}, y + \frac{1}{2}, z$; (b) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; (c) $-x, -y, -z + 1$ for **3**.

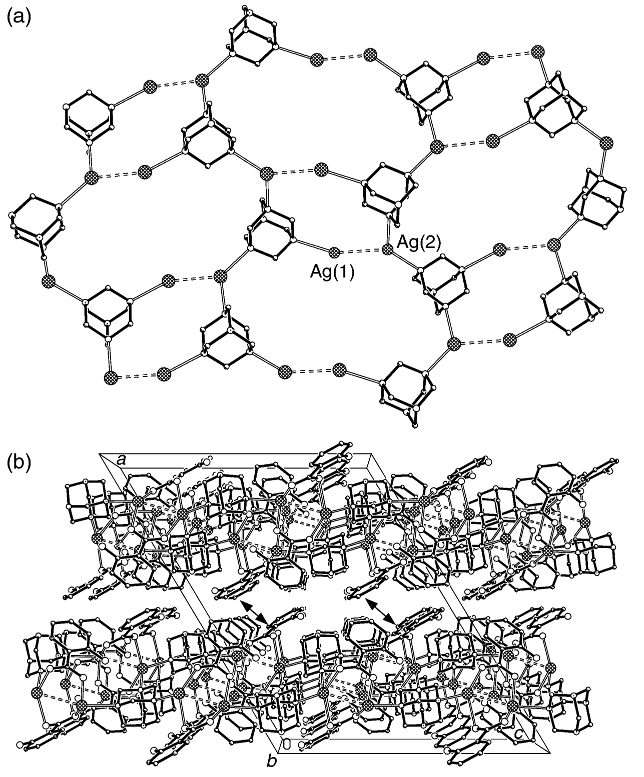

Fig. 2 Perspective views of the layer viewed along the *a* axis (a), and the three-dimensional network viewed along the *b* axis (b) showing the offset face-to-face π–π stacking interaction between the adjacent aromatic rings of the adjacent layers in **2**.

2.433(2) Å, N–Ag–N(or O) 88.50(8)–120.71(7)°] to complete a distorted tetrahedron.

As illustrated in Fig. 1(b), the aromatic groups are slanted up and down the co-ordination layer and the angle between each cin aromatic group and the two-dimensional layers is *ca.* 45°, and the orientations of the adjacent aromatic rings at the same side of the layer are alternately staggered with a dihedral angle of *ca.* 76°. On the other hand, each pair of adjacent aromatic rings from adjacent layers are not parallel, and the two-dimensional layers are stacked through van der Waals interaction between interlayer aromatic rings into a three-dimensional structure with channels, in which the lattice water molecules are clathrated and form donor hydrogen bonds [O(1w)$\cdots$O(2) 2.754(4); O(2w)$\cdots$N(3c) 3.072(5) Å] with the carboxylate oxygen atoms and the unco-ordinated hmt nitrogen atoms.

In **2** the dimeric $Ag_2(sal)_2$ fragments are also bridged by hmt ligands, each using two nitrogen atoms, into infinite chains along the *c*-axis direction, similar to the one-dimensional chains in **1**. On the other hand, the hmt ligands in the chains of **2** are in the common tridentate mode, therefore the one-dimensional chains are further interconnected by ligation of the third nitrogen atom of the μ_3-hmt to one Ag(I) of the dinuclear fragment in an adjacent $[Ag_2(sal)_2(hmt)]_\infty$ chain, which results in the formation of a two-dimensional infinite wavy co-ordination layer with decagonal and small hexagonal units, as illustrated in Fig. 2(a). Each large decagonal unit is organised by six Ag(I) and four hmt ligands, whereas each small hexagonal unit is organised by four Ag(I) and two hmt ligands. Two crystallographically independent Ag(I) have two different co-ordination geometries. Each Ag(1) atom is joined to one Ag(2) atom by two μ-carboxylate bridges [Ag(1)–O 2.262(4) and 2.316(4) Å] with an Ag$\cdots$Ag distance of 3.042(1) Å, indicating a weak interaction;[20] and the Ag(1) atom is further ligated by one nitrogen atom from the hmt ligand to furnish a T-shaped geometry [Ag(1)–N(1) 2.426(4) Å]. Besides the ligation of two oxygen atoms of the μ-carboxylate bridges [Ag(2)–O 2.279(4) and 2.387(4) Å], the Ag(2) atom is further ligated by two nitrogen atoms from two different hmt ligands to exhibit a distorted tetrahedral geometry [Ag(2)–N 2.338(4)–2.376(4) Å; N–Ag(2)–N(or O) 91.4(2)–125.8(1)°].

Similar to **1**, the aromatic groups in **2** are slanted up and down the layer (Fig. 2(b)), and the orientations of the adjacent aromatic rings at the same side of the layer are alternately staggered with a dihedral angle of 125°. The two-dimensional layers are extended into three-dimensional networks through the moderately strong, offset π–π stacking interaction between the aromatic rings from adjacent layers with a face-to-face distance of *ca.* 3.60 Å.

It is noteworthy that no two-dimensional Ag–hmt network consisting of dimeric silver(I) fragments has been found before

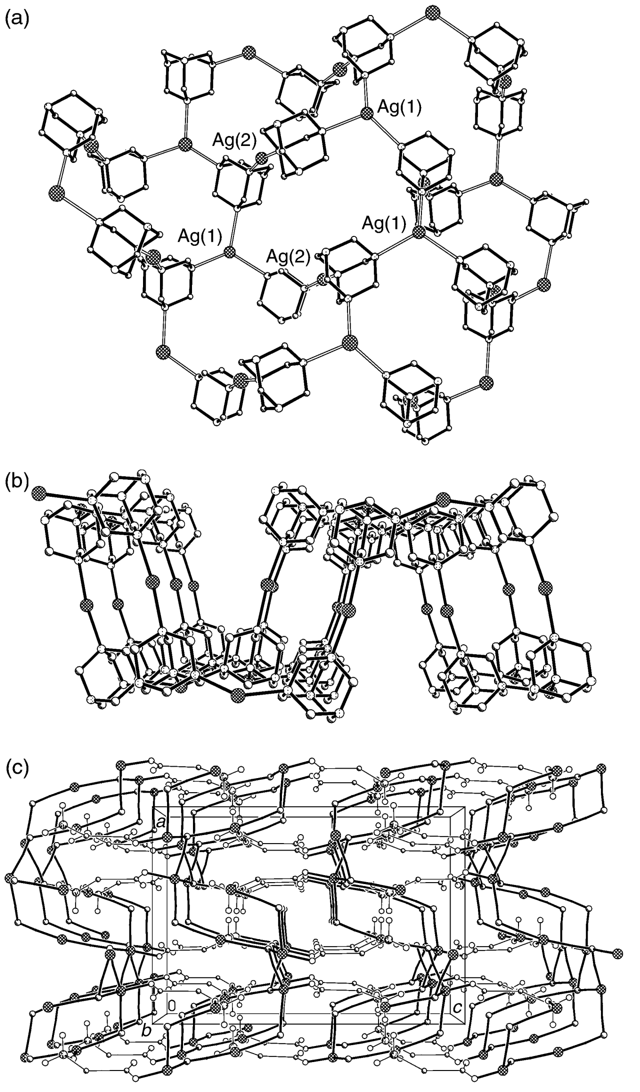

Fig. 3 Perspective views of the layer viewed from the top (a) and side (b) and the three-dimensional network viewed along the *b* axis (c) in **3**. For clarity, the hmt ligands and the ssa aromatic rings are simplified as open balls at their centres of mass.

this work. Therefore the two-dimensional nets in **1** and **2** represent two new topological motifs of two-dimensional Ag–hmt nets featuring dimeric silver(I) fragments.

Complex **3** consists of another new type of two-dimensional infinite highly undulated Ag–hmt layers with irregular decagonal units, which are significantly non-coplanar, as illustrated in Fig. 3(a). The decagonal unit may be symbolised as a rectangular unit (Scheme 2(C)), which is organised by five Ag(I) in two types of geometries and five hmt molecules in two types of bridging modes. The Ag(1) atom is co-ordinated in a distorted tetrahedral geometry by three nitrogen atoms from three hmt ligands [Ag(1)–N 2.339(5)–2.409(5) Å; N–Ag(1)–N 111.2(2)–116.0(2)°] and one oxygen atom from a monodentate ssa carboxylate group [Ag(1)–O 2.461(6) Å; N–Ag(1)–O 85.7(2)–132.7(2)°]; while the Ag(2) atom is in a T-shaped geometry ligated by two nitrogen atoms from two hmt ligands and one oxygen atom from a monodentate ssa sulfonate group [Ag(2)–N 2.178(5) and 2.196(5), Ag(2)–O 2.493(6) Å; N–Ag(2)–N 169.6(2), N–Ag(2)–O 92.1(2) and 96.2(2)°]. It should be noted that five hmt ligands in a unit exhibit two different bridging modes in each structural unit, of which three are in a μ_3-bridging mode and two are in a μ-bridging mode. To our knowledge, hmt was always found to act in a unique bridging mode in each two-dimensional Ag–hmt layer.[6–8,11–13] Therefore, **3** is the first example constructed by mixed μ- and μ_3-bridging hmt ligands in a two-dimensional Ag–hmt layer, though a similar mixed bridging mode has been found in a one-dimensional ribbon-like co-ordination polymer $[Ag_2(\mu\text{-hmt})(\mu_3\text{-hmt})(H_2O)(SbF_6)]$.[7]

The two-dimensional layers in **3** are highly undulated that the layer thickness is *ca.* 9.3 Å, as shown in Fig. 3(b). As the ssa ligands function as bidentate bridges using both of the carboxylate and sulfonate ends in co-ordination to the Ag(I) and orientate up and down the Ag–hmt layers, they interconnect the adjacent two-dimensional layers to generate a three-dimensional structure, as shown in Fig. 3(c).

It is noteworthy that, from the topological point of view, the two-dimensional layers in **1** and **3** can be rationalised as the same topology, a 3-connected net with (6,6) topology, comprised of six connected nodes shared by seven hexagons in **1** or seven decagons in **3**. The minor difference is that, in **1**, the hmt ligands only act as spacers and the Ag(I) are employed as 3-connected centres (Scheme 2(A)); while in **3** some hmt ligands are 3-connected centres and the other ones act as spacers, and similarly some of the Ag(I) act as 3-connected centres and the others as spacers (Scheme 2(C)). On the other hand, **2** is a complex with $(4,8^2)$ topology, since Ag(1) atoms in the dimeric cores, in fact, act as spacers. This type of net was predicted by Wells[22] and has recently been documented in one silver(I) and one lanthanide complex.[23]

Conclusion

We have successfully synthesized three new Ag–hmt complexes, which exhibit different and unprecedented topological motifs of Ag–hmt layers. Among them **1** is the first two-dimensional Ag–hmt net constructed with μ-hmt ligands as spacers. Both **1** and **2** are the first two-dimensional Ag–hmt nets constructed with dimeric silver(I) fragments, whereas **3** is the first two-dimensional Ag–hmt net constructed with mixed μ- and μ_3-bridging hmt ligands. The present work suggests an effective route to construct two-dimensional Ag–hmt nets consisting of dimeric silver(I) fragments.

Acknowledgements

This work was supported by the NSFC (grant no. 29971033 and 20001008) and Foundation for University Key Teacher of the Ministry of Education of China. We also thank the Chemistry Department of the Chinese University of Hong Kong for donation of the diffractometer.

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