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Syntheses and structures of six chain-, ladder- and grid-like co-ordination polymers constructed from μ-hexamethylenetetramine and silver salts

Shao-Liang Zheng, Ming-Liang Tong,* Xiao-Lan Yu and Xiao-Ming Chen*

School of Chemistry and Chemical Engineering, Zhongshan University, Guangzhou 510275, PR China. E-mail: cescxm@zsu.edn.cn

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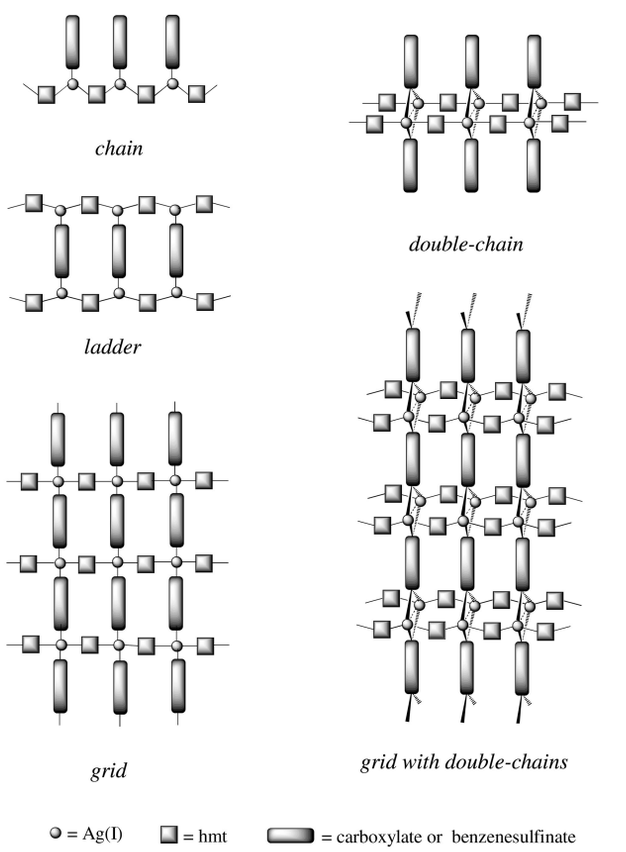
Six interesting co-ordination polymers [Ag(μ-hmt)(hba)(H_2O)] **1**, [Ag(μ-hmt)(aba)(H_2O)] **2**, [Ag_2(μ-hmt)$_2$(bca)-(H_2O)$_2$]·H_2O **3**, [Ag(μ-hmt)(ina)]·0.5H_2O **4**, [Ag(μ-hmt)(bsa)] **5**, [Ag_2(μ-hmt)$_2$(bda)]·4H_2O **6** (hmt = hexamethylenetetramine, hba = 4-hydroxybenzoate, aba = 4-aminobenzoate, bca = 4,4′-biphenyldicarboxylate, ina = isonicotinate, bsa = benzenesulfinate, bda = 1,4-butanedioate), have been prepared and structurally characterised. These co-ordination frameworks, all based on the Ag(μ-hmt) chains, exhibit new structural varieties in the Ag–hmt system, such as the chains in **1** and **2**, ladders in **3**, grids in **4**, double-chains in **5**, as well as rectangular grids with double-chains in **6**. The result shows that the structural variations are mainly dependent upon the nature of the anionic ligands used.

Introduction

Pronounced interest has recently been focused on the crystal engineering of supramolecular architectures organised by co-ordinate covalent bonds or supramolecular contacts (such as hydrogen bonding, π–π interaction *etc.*).[1,2] The self-assembly of these frameworks is highly influenced by factors such as solvent system,[1a] template,[3,4] pH value of the solution[4] and steric requirements of the counter ion.[5] Therefore, much work is required to extend the knowledge of the relevant structural types and establish proper synthetic strategies leading to the desired species. Using a 'building block' methodology, combination of hexamethylenetetramine (hmt) as a polydentate ligand and silver(I) has produced a wide variety of supramolecular architectures.[5–10] In the reported Ag(I)–hmt complexes, the hmt ligands are usually in the μ_3- or μ_4-bridged mode. In contrast, no complex consisting of [Ag(μ-hmt)]$_\infty$ chains has been documented to date, though the μ-hmt co-ordination mode has recently been found in two complexes, namely the oligomeric pentanuclear complex [Ag_5(μ-hmt)$_6$](PF_6)$_8$[5b] and the one-dimensional ribbon-like co-ordination polymer [Ag_2(μ-hmt)-(μ_3-hmt)(H_2O)(SbF_6)].[5e]

In our continuing work on the construction of new structural types of Ag–hmt co-ordination networks, we have established a feasible route to novel frameworks based on [Ag(μ-hmt)]$_\infty$ chains. We now report systematic preparations and crystal structures of a series of co-ordination polymers, namely [Ag(μ-hmt)(hba)(H_2O)] **1**, [Ag(μ-hmt)(aba)(H_2O)] **2**, [Ag_2-(μ-hmt)$_2$(bca)(H_2O)$_2$]·H_2O **3**, [Ag(μ-hmt)(ina)]·0.5H_2O **4**, [Ag(μ-hmt)(bsa)] **5**, [Ag_2(μ-hmt)$_2$(bda)]·4H_2O **6** (hba = 4-hydroxybenzoate, aba = 4-aminobenzoate, bca = 4,4′-biphenyldicarboxylate, ina = isonicotinate, bsa = benzenesulfinate, bda = 1,4-butanedioate). All of these co-ordination networks feature μ-hmt components, as well as new topologic structures, namely *chain* (**1** and **2**), *ladder* (**3**), *grid* (**4**), *double-chains* (**5**) and a *rectangular-grid with double-chains* (**6**), as illustrated in Scheme 1.



Scheme 1 The structural motifs of the co-ordination polymers containing [Ag(μ-hmt)]$_\infty$ chains.

Experimental

Materials

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.

Syntheses

All complexes were synthesised by reaction of Ag_2O with the

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Table 1 Crystal data and structure refinement for complexes **1**–**6**

	1	**2**	**3**	**4**	**5**	**6**
Formula	$C_{13}H_{19}AgN_4O_4$	$C_{13}H_{20}AgN_5O_3$	$C_{26}H_{38}Ag_2N_8O_7$	$C_{12}H_{17}AgN_5O_{2.5}$	$C_{12}H_{17}AgN_4O_2S$	$C_{16}H_{36}Ag_2N_8O_8$
FW	403.19	401.21	790.38	379.18	289.23	684.27
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic	Triclinic
Space group	$P2_1/n$ (no. 14)	*Pmma* (no. 62)	$C2/m$ (no. 12)	*Aba*(2) (no. 41)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	6.491(3)	20.121(10)	21.562(8)	16.139(9)	6.442(3)	6.563(2)
b/Å	20.146(15)	6.4910(10)	6.522(2)	14.005(6)	19.385(13)	9.187(6)
c/Å	11.073.(9)	11.417(6)	11.146(4)	12.626(4)	11.262(8)	10.553(5)
α/°						76.75(2)
β/°	92.34(2)		91.90(2)		100.94(2)	79.47(2)
γ/°						87.49(2)
V/Å^3	1446.8(17)	1491.1(11)	1566.6(9)	2854(2)	1380.8(15)	608.9(5)
Z	4	4	2	8	4	1
D_c/g cm^{-3}	1.851	1.792	1.676	1.765	1.872	1.866
μ(Mo-Kα)/mm^{-1}	1.418	1.373	1.306	1.426	1.618	1.666
No. unique data	3601	1686	1917	2292	3934	3243
No. data with $I > 2\sigma(I)$	3323	1596	1867	2156	3645	3230
R_1 [$I > 2\sigma(I)$]	0.0679	0.0646	0.0493	0.0327	0.0392	0.0414
wR_2 (all data)	0.2415	0.1725	0.1409	0.0876	0.1086	0.1067

appropriate carboxylic acids or sodium benzenesulfinate and hmt in CH_2Cl_2–MeOH–H_2O (v/v 10 : 10 : 1) solution with the addition of aqueous NH_3 solution.

[Ag(μ-hmt)(hba)(H$_2$O)] 1. A CH_2Cl_2–MeOH–H_2O (v/v 10 : 10 : 1) solution (10 cm^3) containing 4-hydroxybenzoic acid (0.14 g, 1.0 mmol), hmt (0.14 g, 1.0 mmol) and Ag_2O (0.16 g, 0.5 mmol) was stirred at 50 °C for 30 min. The mixture dissolved by dropwise addition of aqueous NH_3 solution. The resulting colourless solution was allowed to stand in air at room temperature for a week, yielding colourless crystals in good yield (82%). Anal. calcd. for $C_{13}H_{19}AgN_4O_4$: C, 38.73; H, 4.75; N, 13.90. Found: C, 38.68; H, 4.82; N, 13.75%. IR (KBr, cm^{-1}): 3410s, 3375s, br, 3226m, 2950m, 2886m, 1648s, 1577vs, 1519vs, 1459s, 1407m, 1236vs, 1006vs, 845w, 814m, 782m, 692m, 664w, 623w, 505w.

[Ag(μ-hmt)(nba)(H$_2$O)] 2. Was prepared as for **1** (yield *ca.* 78%). Anal. calcd. for $C_{13}H_{20}AgN_5O_3$: C, 38.82; H, 5.01; N, 17.41. Found: C, 38.78; H, 4.98; N, 17.45%. IR (KBr, cm^{-1}): 3415s, br, 2932w, 2880w, 1698s, 1543vs, 1457w, 1411vs, 1267w, 1236m, 1179w, 1129w, 1006vs, 851w, 814m, 785m, 689m, 620m, 508w.

[Ag$_2$(μ-hmt)$_2$(bca)(H$_2$O)$_2$]·H$_2$O 3. Was prepared as for **1** (yield *ca.* 72%). Anal. calcd. for $C_{26}H_{38}Ag_2N_8O_7$: C, 39.51; H, 4.85; N, 14.18. Found: C, 39.58; H, 4.91; N, 14.15%. IR (KBr, cm^{-1}): 3370s, br, 2954m, 2924m, 2875m, 2243w, 1936w, 1662m, 1584vs, 1535vs, 1460m, 1390vs, 1235vs, 1190m, 1130w, 1047m, 1006vs, 930w, 841m, 816s, 768s, 696m, 674s, 602m, 511m.

[Ag(μ-hmt)(ina)]·0.5H$_2$O 4. Was prepared as for **1** (yield *ca.* 70%). Anal. calcd. for $C_{12}H_{17}AgN_5O_{2.5}$: C, 38.01; H, 4.52; N, 18.47. Found: C, 38.08; H, 4.49; N, 18.55%. IR (KBr, cm^{-1}): 3435m, br, 3001w, 2949m, 2876m, 1640w, 1583vs, 1550vs, 1460m, 1384vs, 1238vs, 1184m, 1091w, 1026w, 1007vs, 838s, 804m, 690s, 665m, 631w, 509m.

[Ag(μ-hmt)(bsa)] 5. Was prepared as for **1** (yield *ca.* 70%), using sodium benzenesulfinate in place of 4-hydroxybenzoic acid. Anal. calcd. for $C_{12}H_{17}AgN_4O_2S$: C, 37.03; H, 4.40; N, 14.39; S, 8.24. Found: C, 36.98; H, 4.38; N, 14.45; S, 8.23%. IR (KBr, cm^{-1}): 3415m, br, 3055w, 2948m, 2919m, 2872m, 1675w, 1629w, 1457m, 1438m, 1236vs, 1080m, 1006vs, 813s, 754m, 693s, 675m, 576m, 511m, 482w.

[Ag$_2$(μ$_2$-hmt)$_2$(bda)]·4H$_2$O 6. Was prepared as for **1** (yield *ca.* 72%). Anal. calcd. for $C_{16}H_{36}Ag_2N_8O_8$: C, 28.09; H, 5.30; N, 16.38. Found: C, 28.05; H, 5.39; N, 16.42%. IR (KBr, cm^{-1}): 3386s, br, 2950m, 2924m, 2875m, 1667m, 1569vs, 1460m, 1400s, 1294w, 1238vs, 1007vs, 924w, 812s, 671s, 510m.

X-Ray crystallography

Diffraction intensities for these six complexes were collected at 21 °C on a Siemens R3m diffractometer using the ω-scan technique. Lorentz-polarization and absorption corrections were applied.[11] The structures were solved by direct methods and refined by the full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs, respectively.[12,13] 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 temperature factors. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[14] The absolute structure for **4** has been determined with a Flack parameter of 0.00(5).[15] 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.[16]

CCDC reference numbers 152791–152796.

See http://www.rsc.org/suppdata/dt/b0/b009068i/ for crystallographic data in CIF or other electronic format.

Results and discussion

Synthesis and characterisation

All the complexes were synthesised by reaction of Ag_2O with the appropriate carboxylic acids or sodium benzenesulfinate and hmt in aqueous organic solution with dropwise addition of aqueous NH_3 solution. Compared with the synthesis of the related complexes[5–10] using appropriate silver salts, the utilization of Ag_2O, appropriate carboxylic acids and hmt, followed by dropwise addition of aqueous NH_3 solution in this work, produced a complex system, which may play an important role in the construction of frameworks based on the $[Ag(\mu\text{-hmt})]_\infty$ chains.

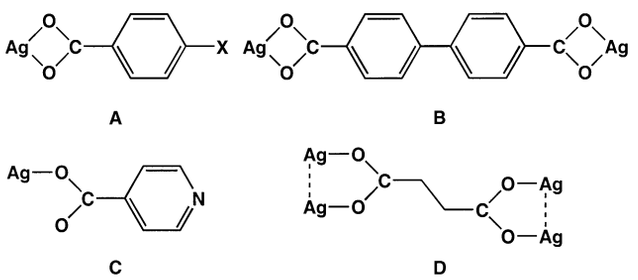
In general the IR spectra show features attributable to each component of the complexes. For complex **1**, the characteristic bands of the dicarboxylate groups are shown in the usual region at 1577vs cm^{-1} for the antisymmetric stretching and at 1459s cm^{-1} for symmetric stretching. The separation (Δ) between $\nu_{as}(CO_2)$ and $\nu_{sym}(CO_2)$ is 118 cm^{-1}. For complex **2**, the characteristic bands of the dicarboxylate groups are shown at 1543vs cm^{-1} for the antisymmetric stretching and at 1411vs cm^{-1} for symmetric stretching. The Δ value of complex **2** is 132

Table 2 Selected bond lengths (Å) and angles (°) for complexes **1**–**6**

Complex **1**			
Ag(1)–N(3a)	2.389(6)	Ag(1)–O(1w)	2.458(6)
Ag(1)–N(1)	2.395(5)	O(3)···O(2)	2.638(7)
Ag(1)–O(1)	2.556(5)	O(1w)···O(2)	2.851(8)
Ag(1)–O(2)	2.524(5)	O(1w)···O(1)	2.741(7)
N(3a)–Ag(1)–N(1)	115.1(2)	N(1)–Ag(1)–O(1)	92.0(2)
N(3a)–Ag(1)–O(1w)	92.4(2)	O(1w)–Ag(1)–O(1)	102.7(2)
N(1)–Ag(1)–O(1w)	92.3(2)	O(2)–Ag(1)–O(1)	51.2(2)
N(3a)–Ag(1)–O(2)	97.4(2)	O(3)–H···O(2)	133.2
N(1)–Ag(1)–O(2)	130.7(2)	O(1w)–H(1wA)···O(2)	171.2
O(1w)–Ag(1)–O(2)	123.6(2)	O(1w)–H(1wB)···O(1)	164.2
N(3a)–Ag(1)–O(1)	148.5(2)		
Complex **2**			
Ag(1)–N(2a)	2.400(7)	Af(1)–O(1a)	2.546(7)
Ag(1)–N(2)	2.400(7)	Ag(1)–O(1)	2.546(7)
Ag(1)–O(1w)	2.457(10)	O(1w)···O(1)	2.743(10)
N(2a)–Ag(1)–N(2)	113.4(3)	N(2a)–Ag(1)–O(1)	143.1(2)
N(2a)–Ag(1)–O(1w)	93.4(2)	N(2)–Ag(1)–O(1)	94.2(2)
N(2)–Ag(1)–O(1w)	93.4(2)	O(1w)–Ag(1)–O(1)	109.6(3)
N(2a)–Ag(1)–O(1a)	94.2(2)	O(1a)–Ag(1)–O(1)	51.5(3)
N(2)–Ag(1)–O(1a)	143.1(2)	O(1w)–H(1w)···O(1)	139.1
O(1w)–Ag(1)–O(1a)	109.6(3)		
Complex **3**			
Ag(1)–N(1)	2.408(4)	Ag(1)–O(1a)	2.500(4)
Ag(1)–N(1a)	2.408(4)	Ag(1)–O(1wb)	2.477(6)
Ag(1)–O(1)	2.500(4)	O(1)···O(1w)	2.710(6)
N(1)–Ag(1)–N(1a)	114.7(2)	O(1wb)–Ag(1)–O(1a)	115.5(2)
N(1)–Ag(1)–O(1wb)	92.7(1)	N(1)–Ag(1)–O(1)	93.6(2)
N(1a)–Ag(1)–O(1wb)	92.7(1)	N(1a)–Ag(1)–O(1)	139.4(1)
N(1)–Ag(1)–O(1a)	139.4(1)	O(1wb)–Ag(1)–O(1)	115.5(2)
N(1a)–Ag(1)–O(1a)	93.6(2)	O(1a)–Ag(1)–O(1)	48.8(2)
O(1w)–H(1w)···O(1)	159.8		
Complex **4**			
Ag(1)–N(1a)	2.309(4)	Ag(1)–N(2)	2.404(4)
Ag(1)–N(5b)	2.361(4)	O(1w)···O(1)	2.792(7)
Ag(1)–O(2)	2.396(4)		
N(1a)–Ag(1)–N(5b)	122.5(2)	N(1a)–Ag(1)–N(2)	101.3(2)
N(1a)–Ag(1)–O(2)	103.9(2)	N(5b)–Ag(1)–N(2)	112.6(1)
N(5b)–Ag(1)–O(2)	92.7(2)	O(2)–Ag(1)–N(2)	128.6(2)
O(1w)–H(1w)···O(1)	165.1		
Complex **5**			
Ag(1)–O(1)	2.357(3)	Ag(1)–O(2b)	2.446(4)
Ag(1)–N(1)	2.364(3)	A(1)···Ag(1b)	3.085(2)
Ag(1)–N(3a)	2.445(3)		
N(1)–Ag(1)–N(3a)	111.8(1)	O(1)–Ag(1)–N(3a)	98.1(1)
O(1)–Ag(21)–O(2b)	118.6(1)	N(1)–Ag(1)–O(2b)	106.8(1)
O(1)–Ag(1)–N(1)	127.1(1)	N(3a)–Ag(1)–O(2b)	85.4(1)
Complex **6**			
Ag(1)–O(1a)	2.355(3)	O(2)···O(2w)	2.830(5)
Ag(1)–N(3b)	2.390(3)	O(1w)···O(2w)	2.805(6)
Ag(1)–O(2)	2.400(3)	O(1w)···N(4d)	2.923(6)
Ag(1)–N(1)	2.411(3)	O(2w)···O(1c)	2.754(5)
Ag(1)–Ag(1a)	2.944(1)		
O(1a)–Ag(1)–N(3b)	113.4(1)	N(3b)–Ag(1)–Ag(1a)	93.54(9)
O(1a)–Ag(1)–O(2)	131.9(1)	O(2)–Ag(1)–Ag(1a)	72.65(9)
N(3b)–Ag(1)–O(2)	104.5(1)	N(1)–Ag(1)–Ag(1a)	145.0(1)
O(1a)–Ag(1)–N(1)	96.9(1)	O(1w)–H(1wA)···O(2w)	168.3
N(3b)–Ag(1)–N(1)	117.4(1)	O(1w)–H(1wB)···N(4d)	164.7
O(2)–Ag(1)–N(1)	90.7(1)	O(2w)–H(2wA)···O(2)	148.5
O(1a)–Ag(1)–Ag(1a)	76.4(1)	O(2w)–H(2wB)···O(1c)	150.7

Symmetry codes: (a) $x-1$, y, z for **1**; (a) x, $-y+1/2$, z for **2**; (a) x, $-y+1$, z, (b) $-x+3/2$, $-y+3/2$, $-z$ for **3**; (a) $x+1/2$, $-y+3/2$, z, (b) $-x+3/2$, y, $z+1/2$ for **4**; (a) $x+1$, y, z, (b) $-x-1$, $-y+1$, $-z+1$ for **5**; (a) $-x$, $-y$, $-z+1$, (b) $x-1$, y, z, (c) $x+1$, y, z, (d) $-x+1$, $-y+1$, $-z+1$ for **6**.

cm^{-1}. For complex **3**, the characteristic bands of the dicarboxylate units are shown in the usual region at 1535vs cm^{-1} for the antisymmetric stretching and at 1390vs cm^{-1} for symmetric stretching. The Δ value of complex **3** is 145 cm^{-1}. For complex **4**, the characteristic bands of the dicarboxylate units are shown in the usual region at 1583vs cm^{-1} for the antisymmetric stretching and at 1384vs cm^{-1} for symmetric stretching. The Δ value of complex **4** is 199 cm^{-1}. For complex **6**, the characteristic bands of the dicarboxylate units are shown in the usual region at 1569vs cm^{-1} for the antisymmetric stretching and at 1400s cm^{-1} for symmetric stretching. The Δ value of complex **6** is 169 cm^{-1}. The splittings of $\nu_{as}(CO_2)$ in these complexes indicates that the carboxylate groups function in different co-ordination fashions (Scheme 2),[17] in agreement with the crystal structures of complexes **1**–**4** and **6**.



Scheme 2 The co-ordination modes of carboxylates: (A) chelate; (B) bis-bidentate; (C) monodentate; (D) bis-bidentate bridging.

Crystal structures

The structure of **1** consists of infinite zigzag $[Ag(\mu\text{-hmt})]_\infty$ chains, with pairs of racemic chains running parallel to the *a*-axis. As illustrated in Fig. 1(a), the Ag(I) atom is in a distorted tetragonal-pyramidal geometry co-ordinated by two nitrogen atoms [Ag(1)–N 2.389(6), 2.395(5) Å] from different hmt ligands, two oxygen atoms [Ag(1)–O 2.524(5), 2.556(5) Å] from a bidentate hba ligand, which form the bottom of the tetragonal pyramid [N–Ag(1)–N 115.1(2)°, O–Ag(1)–N 92.0(2), 97.4(2)°, O–Ag(1)–O 51.2(2)°, Σ_{Ag} 355.7°], and one aqua ligand [Ag(1)–O(1w) 2.458(6) Å, O(1w)–Ag(1)–N(or O) 92.3(2)–123.7(2)°]. The chelate mode of the carboxylate in co-ordination to the Ag(I) atom is rarely documented, in contrast to the commonly reported monodentate and μ-bridging modes.[18] It should be noted that each pair of racemic chains are linked with double hydrogen bonds between the aqua ligands and co-ordinated carboxylate oxygen atoms [O(1w)···O 2.741(7) Å], and extended to a three-dimensional network *via* the hydrogen bonds between the hydroxyl oxygen atoms and the co-ordinated carboxylate oxygen atoms [O(1w)···O 2.851(8) Å] in another adjacent pair of racemic chains, as shown as Fig. 1(b). It is notable that such a single chain structure has not been reported so far, although the Ag(I)–hmt system has been quite extensively investigated.

The structure of **2** is very similar to that of **1**, and consists of zigzag $[Ag(\mu\text{-hmt})]_\infty$ chains, with pairs of racemic chains running parallel to the *a*-axis. The Ag(I) atom is in a distorted tetragonal-pyramidal geometry ligated by two nitrogen atoms [Ag(1)–N 2.400(7) Å] from different hmt ligands, two oxygen atoms [Ag(1)–O 2.546(7) Å] from a chelate nba ligand, which form the bottom of the tetragonal pyramid [N–Ag(1)–N 113.4(3)°, O–Ag(1)–N 94.2(2)°, O–Ag(1)–O 51.5(3)°, Σ_{Ag} 353.3°], and one aqua ligand [Ag(1)–O(1w) 2.457(10) Å, O(1w)–Ag(1)–N(or O) 93.4(2), 109.6(3)°]. Each pair of racemic chains are linked with the hydrogen bonds between the aqua ligands and the co-ordinated carboxylate oxygen atoms [O(1w)···O 2.743(10) Å], resulting in a three-dimensional network. Different from **1**, the hydrogen bond between the amine nitrogen atom and co-ordinated carboxylate oxygen atom is very weak [N···O 3.117(12) Å].

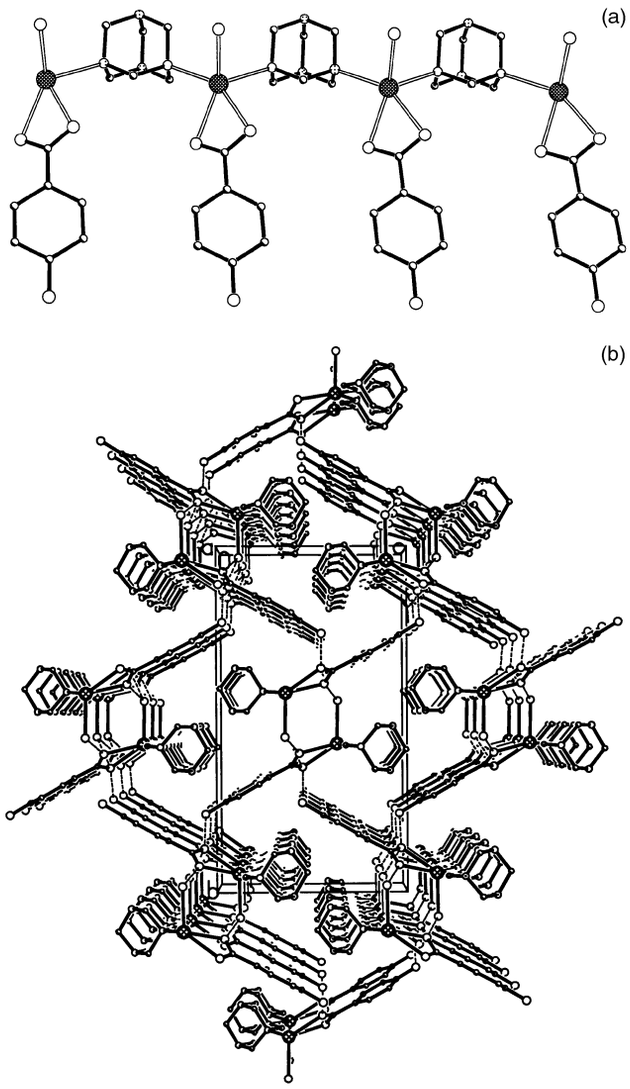


Fig. 1 Perspective view of the chain (a) and hydrogen bonded 3-D network viewed along the *a*-axis (b) in **1**.

Using a dicarboxylate (bca) in place of the monocarboxylate in complex **1** or **2** results in a molecular ladder-like structure in complex **3**, in which the neutral infinite ladder features hmt ligands as the supports and bca ligands as the rungs. As illustrated in Fig. 2(a), two adjacent zigzag $[Ag(\mu\text{-hmt})]_\infty$ chains, which are very similar to those found in **1** and **2**, are interlinked by chelating bis-bidentate bca ligands to form the ladder. The chelate mode of the carboxylate in co-ordination to the Ag(I) atom, as mentioned above, is rarely documented. It should be pointed out that no analogous ladder structure has been documented in the Ag(I)–hmt system previously. The Ag(I) atom is in a greatly distorted square-pyramidal geometry. The basal plane is formed by two nitrogen atoms from different hmt ligands and two oxygens from the bidentate bca ligand [Ag(1)–N 2.408(4), Ag(1)–O 2.500(4) Å; N–Ag(1)–N 114.7(2), O–Ag(1)–N 93.6(2), O–Ag(1)–O 48.8(2)°, Σ_{Ag} 350.7°], and the apical position is occupied by one aqua ligand [Ag(1)–O(1w) 2.477(6) Å, O(1w)–Ag(1)–N(or O) 92.7(1)–115.5(2)°]. The adjacent ladders are linked by hydrogen bonds between the aqua ligands and the co-ordinated carboxylate oxygen atoms [O(1w)···O 2.710(6) Å], resulting in a staircase-like two-dimensional layer along the *b*-axis (see Fig. 2b).

Complex **4** is made up of a two-dimensional neutral rectangular-grid layer and lattice water molecules. As shown in Fig. 3a, the Ag(I) atom is in a distorted tetrahedral geometry co-ordinated by two nitrogen atoms [Ag(1)–N 2.361(4) and 2.404(4) Å, N–Ag(1)–N 112.6(1)°] from different hmt ligands,

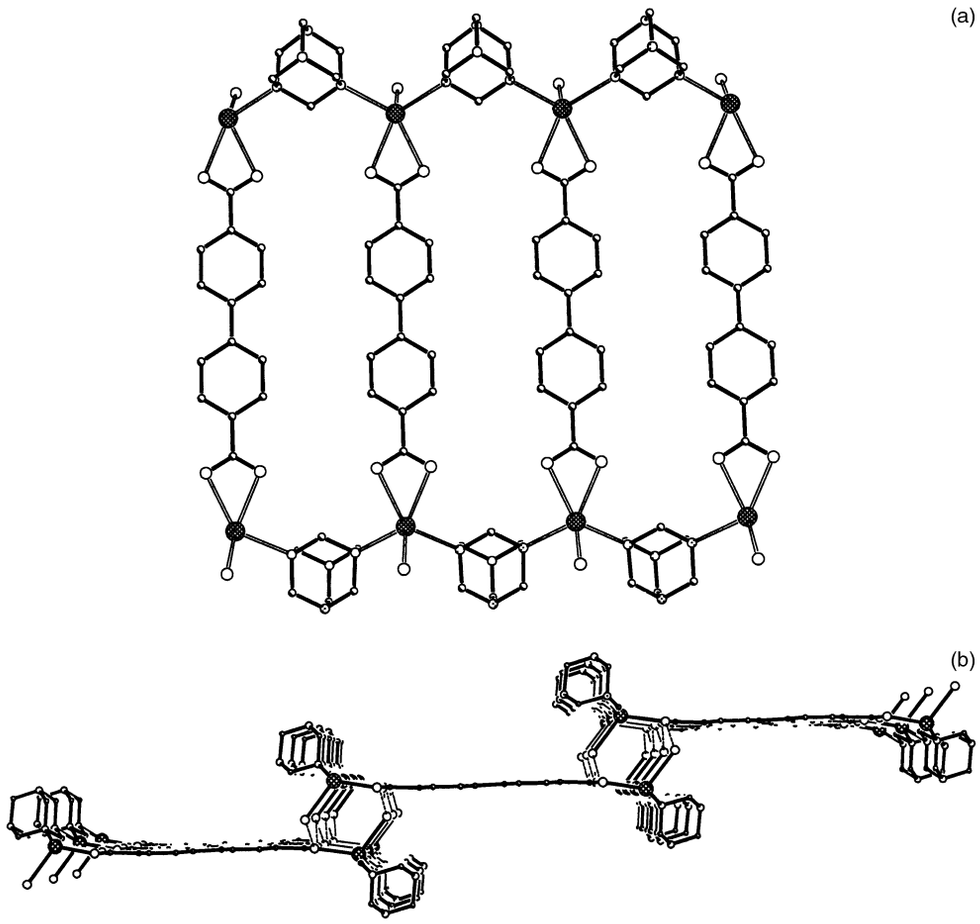


Fig. 2 Top-view of the ladder (a) and side-view of the hydrogen bonded staircase 2-D layer (b) in **3**.

one ina carboxylate oxygen atom [Ag(1)–O 2.396(4) Å, O–Ag(1)–N 92.7(2) and 125.6(2)°] and one pyridyl nitrogen atom [Ag(1)–N 2.309(4) Å, N–Ag(1)–N(or O) 101.3(2)–122.5(2)°] from another ina ligand. The hmt ligand is in a μ-mode, and forms $[Ag(\mu\text{-hmt})]_\infty$ chains, which are similar to those found in **1**–**3**, running along the *c*-axis direction. The ina ligand is in a μ-mode and bridges two Ag(I) atoms in adjacent chains, resulting in a rectangular-grid co-ordination layer along the *b*-axis. The dihedral angle between two pyridyl rings from the ina ligands, which co-ordinate to the same Ag(I), is *ca.* 104° indicating that the layer is arranged in a staircase-like fashion. Adjacent layers are linked into a three-dimensional network through interlayer C–H · · · O hydrogen bonds [C(12) · · · O(2) 3.376 Å; C–H · · · O 142.0°] between the carboxy oxygen atoms and hmt carbon atoms, as shown in Fig. 3b. The lattice water molecules are clathrated between the layers and form two donor hydrogen bonds [O(1w) · · · O(1) 2.792(7) Å] with the unco-ordinated carboxylate oxygen atoms, which also play a role in consolidating the solid-state structure.

Complex **5** consists of double-chains which are made up with a pair of $[Ag(\mu\text{-hmt})]_\infty$ chains linked by μ-bsa ligands running parallel to the *a*-axis, as shown in Fig. 4. In other words, the dimeric $Ag_2(bsa)_2$ fragments are bridged by μ-hmt ligands into an infinite twin-chain. The Ag(I) atoms are joined by two non-coplanar skew–skew μ-sulfinate bridges [Ag(1)–O 2.357(3)–2.446(4) Å; torsion angles Ag–O–S–C 69.7(3)° and −135.7(3)°] with the Ag · · · Ag distance of 3.085(2) Å, indicating a relatively weak Ag · · · Ag interaction.[19] Analogous non-coplanar skew–skew μ-carboxylate bridges have been documented previously.[20] Each Ag(I) atom is further ligated by two nitrogen atoms from two different hmt ligands [Ag(1)–N 2.364(3)–2.445(3) Å, N–Ag(1)–N(or O) 85.4(1) 127.1(1)°], completing a distorted tetrahedron, which is similar to those in the related complex $[Ag_2(\mu_4\text{-hmt})(\mu\text{-}O_2CMe)](MeCO_2)\cdot 4.5H_2O$.[9,10]

Complex **6** is made up of two-dimensional neutral rectangular grids and lattice water molecules. The neutral rectangular grid is unusual since it consists of double chains constructed from a pair of zigzag $[Ag(\mu\text{-hmt})]_\infty$ chains running parallel to the *a*-axis, similar to those in **5**, which are linked by the bis-bidentate μ_4-dba ligands, as shown in Fig. 5. Similarly to **5**, a pair of Ag(I) atoms are joined by two unusual non-coplanar skew–skew μ-carboxylate bridges[9,20] [Ag(1)–O 2.355(3)–2.400(3) Å] with the Ag · · · Ag distance of 2.944 Å, indicating a moderate argentophilic interaction; each Ag(I) atom is further ligated by two nitrogen atoms from two different hmt ligands [Ag(1)–N 2.390(3)–2.411(3) Å; N–Ag(1)–N(or O) 90.7(1)–117.4(1)°)], completing a distorted tetrahedron. The lattice water molecules are clathrated between the layers and form donor hydrogen bonds [O · · · O 2.754(5)–2.830(5) Å; O · · · N 2.923(6) Å] with the co-ordinated carboxylate oxygen atoms and the unco-ordinated hmt nitrogen atoms, extending to a three-dimensional network.

Discussion

We have successfully synthesised a series of Ag–hmt complexes with different anionic ligands in this work, in which the hmt ligands act in the rare μ-bridging co-ordination mode. These complexes exhibit some new structural varieties in the Ag–hmt system, such as *chains* in **1** and **2**, *ladders* in **3**, *grids* in **4**, *double-chains* in **5** and *rectangular-grids with double-chains* in **6**. This work and that of others[21] demonstrates that the complexes may exhibit different, but related, structures by judicious choice of different anionic ligands. The ladder chains in **3** and rectangular-grid layers in **4**, which are similar to the Ag(I) co-

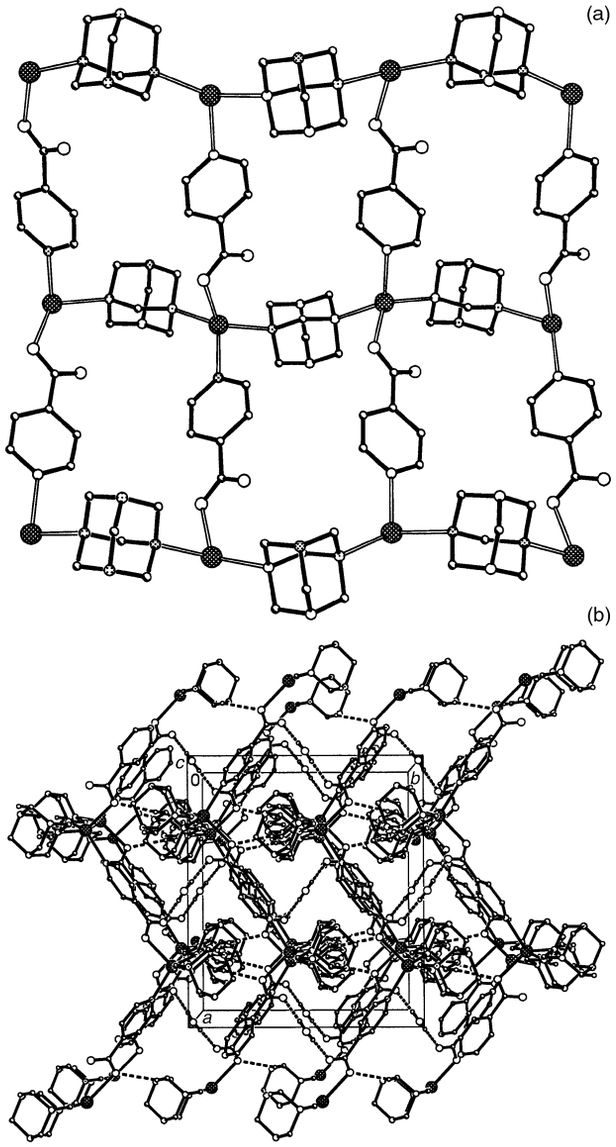


Fig. 3 Perspective view of the 2-D co-ordination rectangular-grid layer viewed along the *b*-axis (a) and the 3-D network viewed along the *c*-axis (b) in **4**.

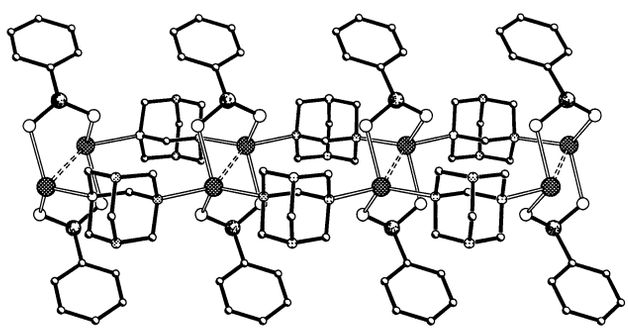


Fig. 4 Perspective view of the double-chain in **5**.

ordination polymers recently reported, respectively,[22] may be regarded as extensions of the single chains in both **1** and **2** by replacement of the chelate monocarboxylate ligands with the bis-monodentate dicarboxylate or μ-*O*,*N*-bridging ina ligands. Similarly, the rectangular-grid with double-chains in **6** may be regarded as an extension of the double-chains in **5** by replacement of the monocarboxylate ligands with the dicarboxylate ligand. On the other hand, the topological differences between **1** (or **2**) and **5**, as well as between **3** and **6**, may be attributed to the different co-ordination behaviour of the carboxylate or

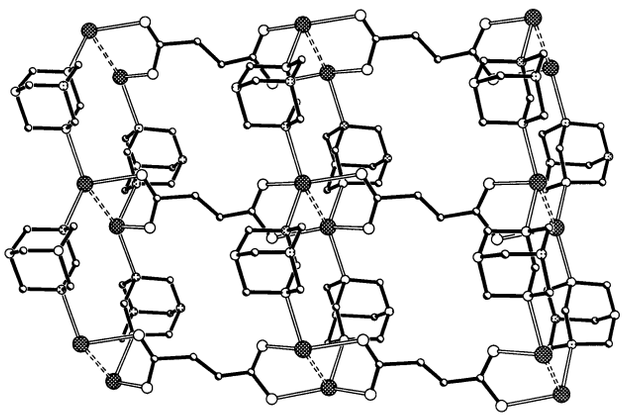


Fig. 5 Perspective view of the rectangular-grid layer with double-chains in **6**.

sulfinate ligands: the chelate mode of the carboxylate results in the single chains in **1** and **2**, whereas the μ-bridging mode of the carboxylate or sulfinate ligands furnishes the double chains in **5** and **6**.

In summary, this work shows that the structural variations are mainly dependent upon the co-ordination properties of the anionic ligands used.

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References

1 (*a*) R. Robson, B. F. Abrahams, S. R. Batten, R. W. Gable, B. F. Hoskins and J. Lieu, *Supramolecular Architecture*, ACS publications, Washington, DC, 1992, p. 256; (*b*) J. M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995, ch. 9; (*c*) S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460; (*d*) O. M. Yaghi, H. Li, C. Davis, D. Richardson and T. L. Groy, *Acc. Chem. Res.*, 1998, **31**, 474; (*e*) M. Munakata, L. Wu and T. Kuroda-Sowa, *Adv. Inorg. Chem.*, 1999, **46**, 173; (*f*) A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby and M. Schröder, *Coord. Chem. Rev.*, 1999, **183**, 117; (*g*) P. J. Hagrman, D. Hagrman and J. Zubieta, *Angew. Chem., Int. Ed.*, 1999, **38**, 2639.
2 C. B. Aakeröy and K. R. Seddon, *Chem. Soc. Rev.*, 1993, 397.
3 (*a*) T. L. Hennigar, D. C. MacQuarrie, P. Losier, R. D. Rogers and M. J. Zaworotko, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 972; (*b*) H. Gudbjartson, K. Biradha, K. M. Poirier and M. J. Zaworotko, *J. Am. Chem. Soc.*, 1999, **121**, 2599.
4 M.-L. Tong, B.-H. Ye, X.-M. Chen and S. W. Ng, *Inorg. Chem.*, 1998, **37**, 2645.
5 (*a*) L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Am. Chem. Soc.*, 1995, **117**, 12861; (*b*) L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *Inorg. Chem.*, 1997, **36**, 1736. (*c*) L. Carlucci, G. Ciani, D. W. V. Gudenberg, D. M. Proserpio and A. Sironi, *Chem. Commun.*, 1997, 631; (*d*) M. Bertelli, L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Mater. Chem.*, 1997, **7**, 1271; (*e*) L. Carlucci, G. Ciani, D. M. Proserpio and S. Rizzato, *J. Solid State Chem.*, 2000, **152**, 211.
6 A. Michelet, B. Voissat, P. Khodadad and N. Rodier, *Acta Crystallogr., Sect. B*, 1981, **37**, 2171.
7 O. M. Yaghi, H. Li and M. O'Keeffe, *Mater. Res. Symp. Proc.*, 1997, **453**, 127.
8 S. R. Batten, B. F. Hoskins and R. Robson, *Inorg. Chem.*, 1998, **37**, 3432.
9 M.-L. Tong, S.-L. Zheng and X.-M. Chen, *Chem. Commun.*, 1999, 561.
10 M.-L. Tong, S.-L. Zheng and X.-M. Chen, *Chem. Eur. J.*, 2000, **6**, 3729.
11 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
12 G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, Göttingen University, Germany, 1997.

13 G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, Göttingen University, Germany, 1997.
14 D. T. Cromer, *International Table for X-Ray Crystallography*, Kluwer Academic Publishers, Dordrecht, 1992. vol. C, Tables 4.2.6.8 and 6.1.1.4.
15 H. D. Flack, *Acta Crystallogr., Sect. A*, 1983, **39**, 876.
16 G. M. Sheldrick, SHELXTL Version 5, Siemens Industrial Automation Inc., Madison, Wisconsin, USA, 1995.
17 (*a*) K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; John Wiley & Sons, New York, 1986; (*b*) J. Tao, M.-L. Tong and X.-M. Chen, *J. Chem. Soc.*, *Dalton Trans.*, 2000, 3666.
18 (*a*) X.-M. Chen and T. C. W. Mak, *J. Chem. Soc.*, *Dalton Trans.*, 1991, 1219; (*b*) X.-M. Chen and T. C. W. Mak, *Polyhedron*, 1991, **10**, 1723; (*c*) W.-Y. Huang, L. Lü, X.-M. Chen and T. C. W. Mak, *Polyhedron*, 1991, **10**, 2687; (*d*) X.-M. Chen and T. C. W. Mak, *J. Chem. Soc.*, *Dalton Trans.*, 1991, 3253; (*e*) X.-M. Chen and T. C. W. Mak, *Aust. J. Chem.*, 1991, **44**, 1783; (*f*) T. C. W. Mak, W. H. Yip and X.-M. Chen, *Inorg. Chim. Acta*, 1993, **203**, 97.
19 (*a*) M. Jansen, *Angew. Chem.*, *Int. Ed. Engl.*, 1987, **26**, 1098; (*b*) P. Pyykkö, *Chem. Rev.*, 1997, **97**, 597; (*c*) M.-L. Tong, X.-M. Chen, B.-H. Ye and L.-N. Ji, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 2237; (*d*) Q. M. Wang and T. C. W. Mak, *J. Am. Chem. Soc.*, 2000, **122**, 7608; (*e*) G. C. Guo, G. D. Zhou and T. C. W. Mak, *J. Am. Chem. Soc.*, 1999, **121**, 3136; (*f*) G. C. Guo and T. C. W. Mak, *Angew. Chem.*, *Int. Ed.*, 1999, **37**, 3268; (*g*) G. C. Guo and T. C. W. Mak, *Angew. Chem.*, *Int. Ed.*, 1998, **36**, 3183.
20 (*a*) Y.-X. Tong, X.-M. Chen and S. W. Ng, *Polyhedron*, 1997, **16**, 3363; (*b*) X.-M. Chen and T. C. W. Mak, *Inorg. Chim. Acta*, 1991, **189**, 3.
21 (*a*) G. L. R. MacGillivray, R. H. Groeneman and J. L. Atwood, *J. Am. Chem. Soc.*, 1998, **120**, 2676; (*b*) S. R. Batten, B. F. Hoskins and R. Robson, *Chem. Eur. J.*, 2000, **6**, 156.
22 (*a*) Y. Suenaga, T. Kuroda-Sowa, M. Maekawa and M. Munakata *J. Chem. Soc.*, *Dalton Trans.*, 2000, 3620; (*b*) L. I. Ino, L.-P Wu, M. Munakata, M. Maekawa, Y. Suenaga, T. Kuroda-Sowa and Y. Kitamori, *Inorg. Chem.*, 2000, **39**, 2746.