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Influence of the counter ions and ligands on structures of silver(I) helicates with di-Schiff bases containing imidazole groups

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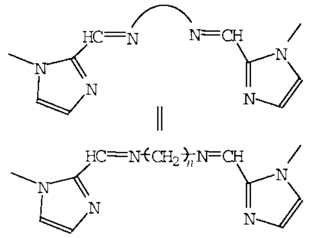
Five complexes, $[Ag_6(bmimen)_5(MeCN)][CF_3SO_3]_6\cdot H_2O$ **1**, $[Ag_7(bmimen)_6][ClO_4]_7\cdot MeCN$ **2**, $[Ag_2(bmimen)_2][NO_3]_2\cdot 0.5H_2O$ **3**, $[Ag_3(bmimpn)_2][CF_3SO_3]_3$ **4** and $[Ag_3(bmimpn)_2]_n[NO_3]_{3n}$ **5**, were obtained by self-assembly of AgX (X = $CF_3SO_3^-$, ClO_4^- or NO_3^-) with bmimen and bmimpn (bmimen = 1,2-bis[(1-methyl-2-imidazolyl)methyleneamino]ethane, bmimpn = 1,3-bis[(1-methyl-2-imidazolyl)methyleneamino]propane). X-Ray single-crystal diffraction shows that bmimen functions in three co-ordination fashions to bridge silver(I) atoms into hexa-, hepta-, and di-nuclear helicates in **1**, **2**, and **3**, respectively. The bmimen ligand can serve in a usual bis(bidentate) fashion with each imidazole-imine bidentate entity chelating a Ag atom, thus bridging a pair of adjacent Ag atoms in **1**, **2** and **3**; it can also act in an unusual tridentate mode with a bidentate entity bridging a pair of adjacent Ag atoms and the imidazole group in another bidentate entity ligating the third Ag atom in **1**, whereas it can also function in another unusual tetradentate mode with a bidentate entity chelating a Ag atom and another bidentate entity bridging another two Ag atoms in **2**. On the other hand, bmimpn acts in two unusual tetradentate fashions to bridge Ag atoms into trinuclear and polymeric helicates in **4** and **5**, respectively. The bmimpn ligand can ligate two Ag atoms, where the di-imine group chelates a Ag atom and two imidazole groups simultaneously bind another Ag atom; it can also ligate three Ag atoms in **5**, in which the two imidazole groups simultaneously bind a Ag atom while each of the two imine groups ligates a Ag atom. The adjacent Ag · · · Ag separations in the cationic chains of **1**, **2**, **4** and **5** are *ca*. 3.0 Å, indicating weak metal–metal interaction, while those in the double helicates of **3** are larger (*ca*. 3.34 Å). The ^1H NMR spectra of **1**, **2** and **3** in solution are virtually identical, as are those of **4** and **5**.

Introduction

The stabilisation of the 5s orbital as a consequence of relativistic effects favours the formation of efficient s/d or s/p hybridisations which are responsible for the significant tendency of heavy metals with d^{10} configuration to form linear two-co-ordinate complexes, gold(I) being the most representative example.[1] In the case of silver(I) relativistic effects are less pronounced than with gold(I) and therefore a greater variety of co-ordination modes is adopted. We and others have found that many factors, such as the nature of the ligands, solvent, steric requirements of anions, *etc*., appear to modulate the stereochemistry of silver(I) complexes. Thus, the co-ordination geometry of silver(I) has been shown to be linear, T-shaped, trigonal, distorted tetrahedral, or octahedral.[2,3]

Schiff bases are excellent chelate ligands, forming a very large number of metal complexes, of which many have structurally been documented.[3a,4] Recently we used imidazole-containing Schiff base ligands in the synthesis of transition metal complexes as structural models of some metalloenzymes.[5] Surprisingly, only a few silver(I) complexes containing multi-Schiff base ligands have been documented for pyridyl imines or macrocyclic imines.[2f,3d,6] As a continuation of our studies on metal–Schiff base complexes, we now report self-assembly of different silver salts with two new di-Schiff base ligands 1,2-bis[(1-methyl-2-imidazolyl)methyleneamino]ethane (bmimen) and 1,3-bis[(1-methyl-2-imidazolyl)methyleneamino]propane (bmimpn) in a 1 : 1 metal : ligand ratio, which yields five oligomeric and polymeric silver(I) helicates with different metal : ligand ratios. More interestingly, the ligands in these complexes exhibit four unusual bridging modes, which have not yet been documented in other silver(I) polymeric helices.[2c,d,f,6a,7]



bmimen $n = 2$
bmimpn $n = 3$

Experimental

All reagents were commercially available and used as received. Solvents were dried by conventional procedures prior to use. All samples were thoroughly dried prior to elemental analyses.

Physical measurements

The C, H, N elemental analyses were performed on a Perkin-Elmer 204 elemental analyser. The IR spectra were recorded on a Nicolet 5DX FT-IR spectrophotometer with KBr discs in the 4000–400 cm^{-1} region, mass spectra (FAB) on a VG ZAB-HS Autospectrophotometer, using 3-nitrobenzyl alcohol as matrix and ^1H NMR spectra on an INOVA 500NB spectrometer with TMS as reference, using CD_3CN as matrix.

CAUTION: although no problems were encountered in the preparation of the perchlorate salts, care should be taken when handing such potentially explosive compounds.

Preparation of ligands and metal complexes

bmimen. To a solution of 1,2-diaminoethane (en) (2 mmol, 0.120 g) in dried MeOH (5 cm^3) was added a solution of 1-

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methylimidazole-2-carbaldehyde (4 mmol, 0.440 g) in dried MeOH (3 cm^3). The mixture was refluxed for 2.5 h, dried with Na_2SO_4, and filtered. The filtrate was evaporated at low pressure, affording a pale yellow powder (*ca.* 75% yield based on en). Calc. for $C_6H_8N_3$: C, 59.00; H, 6.60; N, 34.40. Found: C, 59.34; H, 6.45; N, 34.50%. IR (cm^{-1}): 3275m, 3128m, 3107m, 2952m, 2910m, 2882m, 2846m, 1651s, 1567w, 1525w, 1475s, 1440s, 1363m, 1285m, 1229w, 1152m, 1082w, 1018s, 955w, 927w, 835m, 786s, 709m, 688w, 653w, 554w and 477w. ^1H NMR (500 MHz, CD_3CN): δ 8.23 (2 H, imine), 7.04 (2 H, imidazole ring), 6.98 (2 H, imidazole ring), 3.89 (6 H, CH_3) and 3.88 (4 H, NCH_2).

bmimpn. This was prepared by the procedure described above for bmimen using 1,3-diaminopropane (pn) instead of en. A pale yellow powder was obtained (*ca.* 67% yield based on pn). Calc. for $C_{13}H_{18}N_6$: C, 60.44; H, 7.02; N, 32.53. Found: C, 60.42; H, 6.98, N, 32.61%. IR (cm^{-1}): 3409m, 3107m, 2945m, 2864m, 1651s, 1525w, 1475s, 1440s, 1370w, 1285m, 1229w, 1152w, 1089w, 927w, 765w, 709w, 688w and 568w. ^1H NMR (500 MHz, CD_3CN): δ 8.27 (2 H, imine), 7.05 (2 H, imidazole ring), 7.00 (2 H, imidazole ring), 3.95 (6 H, CH_3), 3.69–3.66 (m, 4 H, NCH_2), 2.02–1.99 (m, 2 H, CH_2).

$[Ag_6(bmimen)_5(MeCN)][CF_3SO_3]_6 \cdot H_2O$ 1. To a solution of en (2 mmol, 0.120 g) in dried MeOH (5 cm^3) was added a solution of 1-methylimidazole-2-carbaldehyde (4 mmol, 0.440 g) in dried MeOH (3 cm^3). The mixture was refluxed for 2.5 h, then a solution of $AgCF_3SO_3$ (2 mmol, 0.520 g) in MeCN (5 cm^3) was added. Colourless crystalline complex **1** was obtained by vapour diffusion of diethyl ether after 3 days (*ca.* 60% yield based on en). Calc. for $C_{68}H_{85}Ag_6F_{18}N_3O_{19}S_6$: C, 28.94; H, 3.04; N, 15.39. Found: C, 29.03; H, 3.15; N, 15.20%. IR (cm^{-1}): 3121w, 2910w, 2853w, 1644m, 1525w, 1489m, 1447m, 1426m, 1349w, 1278s, 1229m, 1166s, 1032s, 948w, 779m, 639s and 519w. MS: *m*/*z* 316 (1%, $[Ag_6(bmimen)_5(MeCN)]^{6+}$). ^1H NMR (500 MHz, CD_3CN): δ 8.44 (2 H, imine), 7.21 (2 H, imidazole ring), 6.96 (2 H, imidazole ring), 4.01 (4 H, NCH_2) and 3.75 (6 H, CH_3).

$[Ag_7(bmimen)_6][ClO_4]_7 \cdot MeCN$ 2. This was prepared by the procedure described for complex **1** using $AgClO_4$ instead of $AgCF_3SO_3$. A colourless crystalline solid of **2** was obtained (*ca.* 55% yield based on en). Calc. for $C_{74}H_{99}Ag_7Cl_7N_{37}O_{28}$: C, 30.04; H, 3.37; N, 17.52. Found: C, 29.86; H, 4.40, N, 17.81%. IR (cm^{-1}): 3121w, 2931w, 2853w, 1637m, 1525w, 1488s, 1440m, 1419m, 1356w, 1285m, 1145m, 1089s, 962w, 779m and 625m. MS: *m*/*z* 317 (1%, $[Ag_7(bmimen)_6]^{7+}$). ^1H NMR (500 MHz, CD_3CN): δ 8.44 (2 H, imine), 7.21 (2 H, imidazole ring), 6.95 (2 H, imidazole ring), 3.99 (4 H, NCH_2) and 3.75 (6 H, CH_3).

$[Ag_2(bmimen)_2][NO_3]_2]_2 \cdot 0.5H_2O$ 3. This was prepared by the procedure described for complex **1** using $AgNO_3$ instead of $AgCF_3SO_3$. The resulting colourless precipitate was recrystallised from a mixture of MeOH, MeCN and CH_2Cl_2 (10 cm^3, 3 : 1 : 1 v/v) by vapour diffusion of diethyl ether, affording crystals of **3** (*ca.* 45% yield based on en). Calc. for $C_{24}H_{33}Ag_2N_{14}O_{6.5}$: C, 34.43; H, 3.97; N, 23.42. Found: C, 34.87; H, 3.98; N, 23.35%. IR (cm^{-1}): 3458m, 3107m, 2924w, 2860w, 1637s, 1482s, 1440s, 1384s, 1285s, 1166w, 1089w, 1046m, 955w, 913w, 828w, 772m, 709w and 575w. MS: *m*/*z* 351 (100%, $[Ag_2(bmimen)_2]^{2+}$). ^1H NMR (500 MHz, CD_3CN): δ 8.44 (2 H, imine), 7.20 (2 H, imidazole ring), 6.96 (2 H, imidazole ring), 3.95 (4 H, NCH_2) and 3.76 (6 H, CH_3).

$[Ag_3(bmimpn)_2][CF_3SO_3]_3$ 4. This was prepared by the procedure described for complex **1** using pn instead of en. A colourless crystalline solid of **4** was obtained (*ca.* 75% yield based on pn). Calc. for $C_{29}H_{36}Ag_3F_9N_{12}O_9S_3$: C, 28.28; H, 2.95; N, 9.10; S, 7.81. Found: C, 28.32; H, 3.05; N, 9.40; S, 7.93%. IR (cm^{-1}): 3128w, 2931w, 2839w, 1644m, 1525w, 1482m, 1440m, 1257s, 1166s, 1089w, 1032s, 955w, 864w, 772m, 702w, 639s, 575w and 519m. MS: *m*/*z* 279 (1.5%, $[Ag_3(bmimpn)_2]^{3+}$). ^1H NMR (500 MHz, CD_3CN): δ 8.40 (2 H, imine), 7.28 (2 H, imidazole ring), 7.11 (2 H, imidazole ring), 3.90–3.89 (m, 4 H, NCH_2), 3.82 (6 H, CH_3) and 2.09–2.04 (m, 2 H, CH_2).

$[Ag_3(bmimpn)_2]_{3n}[NO_3]_{3n}$ 5. This was prepared by the procedure described for complex **1** using pn and $AgNO_3$ instead of en and $AgCF_3SO_3$, respectively. The resulting colourless precipitate was recrystallised from a mixture of MeOH, MeCN, DMF and CH_2Cl_2 (10 cm^3, 3 : 3 : 2 : 2 v/v) by vapour diffusion of diethyl ether, affording crystals of **5** (*ca.* 35% yield based on pn). Calc. for $C_{26}H_{36}N_{15}Ag_3O_9$: C, 30.43; H, 3.54; N, 20.47. Found: C, 30.11; H, 3.44; N, 20.60%. IR (cm^{-1}): 3444w, 3107m, 2938w, 2917w, 2846w, 1644m, 1560w, 1532w, 1482s, 1440s, 1384s, 1285s, 1159w, 1053m, 948w, 779m and 702w. MS: *m*/*z* 279 (1.5%, $[Ag_3(bmimpn)_2]^{3+}$). ^1H NMR (500 MHz, CD_3CN): δ 8.41 (2 H, imine), 7.26 (2 H, imidazole ring), 7.12 (2 H, imidazole ring), 3.94–3.91 (m, 4 H, NCH_2), 3.82 (6 H, CH_3) and 2.08 (m, 2 H, CH_2).

X-Ray crystallography

Diffraction intensities for complexes **1**, **2**, **4** and **5** were collected on a Siemens R3m diffractometer at 293 K using the ω-scan technique. Lorentz-polarisation and absorption corrections were applied.[8] Diffraction intensities for **3** were collected (hemisphere technique) on a Bruker SMART Platform CCD diffractometer at 293 K, and an absorption correction was applied with the SADABS program.[9] The structure solution and full-matrix least-squares refinement based on F^2 were performed with the SHELXS 97 and SHELXL 97[10] program packages, respectively. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the organic ligands were generated geometrically (C–H 0.96 Å) and those of the aqua ligands located from the difference maps; all hydrogen atoms were assigned the same isotropic thermal parameters and included in the structure-factor calculations. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion correction incorporated.[11] The crystallographic data for the five complexes are summarised in Table 1. Selected bond distances and angles are given in Table 2.

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See http://www.rsc.org/suppdata/dt/b0/b002837l/ for crystallographic files in .cif format.

Results

Crystal structures

(a) $[Ag_6(bmimen)_5(MeCN)][CF_3SO_3]_6 \cdot H_2O$ 1. The crystal structure of complex **1** consists of discrete hexanuclear $[Ag_6(bmimen)_5(MeCN)]^{6+}$ cations, $CF_3SO_3^-$ anions and lattice water molecules. The cation is shown in Fig. 1, which shows that it is a helical chain with both ends in a double-helical fashion. Each Ag atom is co-ordinated to imidazole or imine nitrogen atoms from two different ligands, resulting in highly distorted Y-shaped co-ordination geometry except for Ag(3), which is in a highly distorted tetrahedral co-ordination geometry due to ligation of an acetonitrile nitrogen atom. The adjacent Ag···Ag separations in the cation are in the range of 2.9214(14) to 3.1568(15) with the shortest and longest ones for Ag(5)···Ag(3) and Ag(3)···Ag(2), respectively. The Ag···Ag distances are in the range [2.9144(8)–3.2365(5) Å] previously reported in other silver(I) complexes,[3,7a,12] and are well below the summed van der Waals radii of two silver atoms (3.44 Å),[13] indicating weak metal–metal interaction. Within the cation, the metal atoms are arranged in a zigzag fashion with the Ag···Ag···Ag angles in the range of 135.93(5) to 168.07(4)°. It is worthy of note that two of the five bmimen ligands act similarly in an unusual tridentate mode with an

Table 1 Crystal data and structure refinement for complexes **1**, **2**, **3**, **4** and **5**[a]

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{68}H_{85}Ag_6F_{18}N_{31}O_{19}S_6$	$C_{74}H_{99}Ag_7Cl_7N_{37}O_{28}$	$C_{24}H_{33}Ag_2N_{14}O_{6.5}$	$C_{29}H_{36}Ag_3F_9N_{12}O_9S_3$	$C_{26}H_{36}Ag_3N_{15}O_9$
Formula weight	2822.25	2958.08	834.90	1287.49	1026.31
Space group	$P2_1/c$	$C2/c$	$P2_1/c$	$C2/c$	$P2_1/c$
a/Å	14.484(7)	14.587(4)	13.677(3)	24.535(6)	10.308(4)
b/Å	20.380(8)	25.035(6)	27.472(6)	14.760(4)	22.628(10)
c/Å	34.711(10)	30.719(4)	27.311(5)	13.575(2)	15.081(3)
β/°	90.970(10)	101.600(10)	92.820(4)	116.300(10)	90.85(13)
V/Å^3	10245(7)	10894(4)	10249(4)	4407(2)	3517(2)
Z	4	8	12	4	4
μ(MoKα)/cm^{-1}	1.356	1.478	1.646	1.940	1.727
Measured reflections	15260	10795	14714	4344	6194
Observed reflections	7652	5527	10870	2887	3373
$R1$ ($I > 2\sigma$)	0.0831	0.0680	0.0685	0.0525	0.0610
$wR2$ (all data)	0.1707	0.1422	0.0906	0.0897	0.1352

[a] Detail in common: monoclinic.

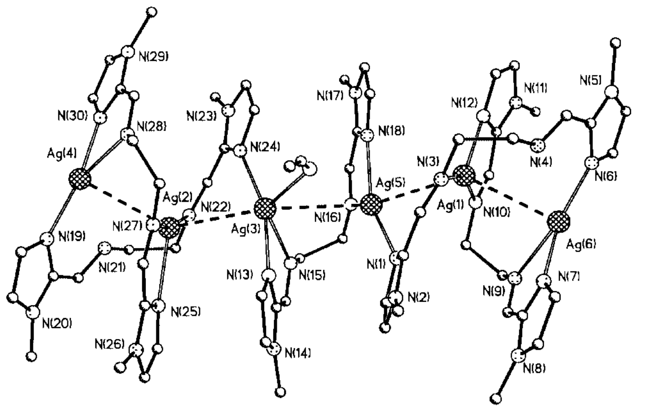

Fig. 1 Perspective view of the hexanuclear cation in complex **1**.

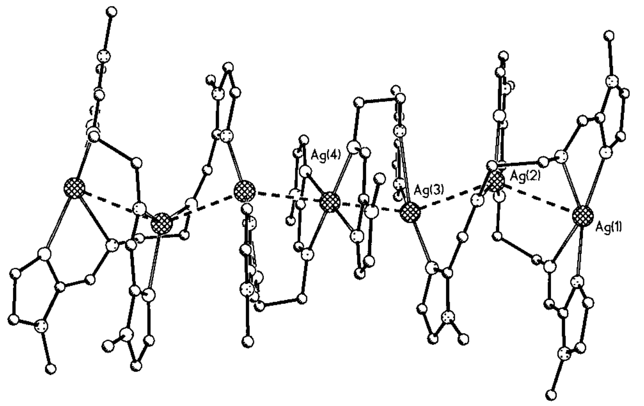

Fig. 2 Perspective view of the heptanuclear cation in complex **2**.

imidazole-imine bidentate entity bridging a pair of metal atoms (Ag(2) and Ag(3); Ag(1) and Ag(5)) and the imidazole group in another bidentate entity ligating the third metal atom (Ag(4) or Ag(6)), as shown in Fig. 1 and Chart 1(a), whereas each of the remaining bmimen acts in a bis(bidentate) fashion to chelate two Ag atoms (Ag(1) and Ag(6); Ag(3) and Ag(5); Ag(2) and Ag(4), respectively), as shown in Fig. 1 and Chart 1(b). To our knowledge, no tridentate bridging mode for di-Schiff bases has been documented in the literature. In the hexanuclear cation the Ag–N bond lengths are in the range of 2.156(8) to 2.600(14) Å, in which the longest one is for the Ag^I–acetonitrile interaction, indicating weak bonding between the solvent molecule and the metal atom; the shortest one is for a co-ordinate bond between a metal atom and an imidazole group. The fact that the average bond distance of Ag–N$_{imidazole}$ (2.233 Å) is shorter than that of Ag–N$_{imine}$ (2.357 Å) also implies a stronger co-ordination ability of an imidazole group in comparison to that of an imine group.

The lattice water molecule forms hydrogen bonds with oxygen atoms of the anions (O(1w)···O(14) 2.819(8), O(1w)···O(17) 2.586(8) Å). The oxygen atoms of the anions have weak contacts with the organic carbon atoms (closest C···O distances being *ca.* 3.2 Å) and no significant contact has been found between the metal atoms and the anions. It is interesting that there are significant π–π stacking interactions between the adjacent imidazole rings within the cation. The adjacent imidazole rings are approximately parallel to each other with dihedral angles at 5 to 20° and face-to-face distances of 3.23 to 3.63 Å, and such π–π stacking interactions may possibly play a role in the formation of the helical structure.

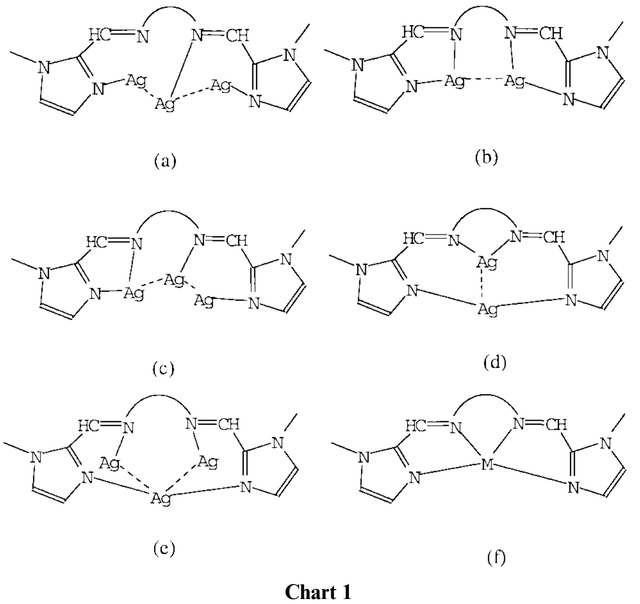

Chart 1

(b) [Ag$_7$(bmimen)$_6$][ClO$_4$]$_7$·MeCN 2. The crystal structure of complex **2** consists of heptanuclear [Ag$_7$(bmimen)$_6$]$^{7+}$ cations, perchlorate anions and solvate acetonitrile molecules. Similar to that in **1**, the heptanuclear cation (see Fig. 2) is also a helical chain with both ends in double-helical arrangement. The atom Ag(4), being located at a crystallographic inversion centre, is co-ordinated by four nitrogen atoms in a distorted square-planar fashion with *cis* N–Ag–N at 70.9(2) or 109.1(2)°; such coplanar four-co-ordination is rarely observed.[14] On the other hand, Ag(1) is in an irregular four-co-ordination environment, while Ag(2) and Ag(3) are in distorted Y-shaped environments. The Ag–N bond lengths are in the range of 2.148(6)–2.619(6) Å. The adjacent Ag···Ag separations in the cation fall in the range of 2.9142(9)–2.9911(8) Å, and the metal atoms are arranged in a zigzag fashion with Ag···Ag···Ag angles in the range of 125.59(3) to 180°. As in the case of **1**, the Ag···Ag

Table 2 Selected bond lengths [Å] and bond angles [°] for the five complexes

1							
Ag(1)–N(3)	2.197(7)	Ag(1)–N(10)	2.288(7)	N(3)–Ag(1)–N(10)	154.8(3)	N(3)–Ag(1)–N(12)	131.4(3)
Ag(1)–N(12)	2.365(8)	Ag(2)–N(22)	2.198(7)	N(10)–Ag(1)–N(12)	73.5(3)	N(22)–Ag(2)–N(27)	166.3(3)
Ag(2)–N(27)	2.253(7)	Ag(2)–N(25)	2.454(8)	N(22)–Ag(2)–N(25)	120.3(3)	N(27)–Ag(2)–N(25)	72.5(3)
Ag(3)–N(24)	2.177(8)	Ag(3)–N(13)	2.211(8)	N(24)–Ag(3)–N(13)	162.5(3)	N(24)–Ag(3)–N(15)	111.5(3)
Ag(3)–N(15)	2.525(8)	Ag(3)–N(31)	2.600(14)	N(13)–Ag(3)–N(15)	72.3(3)	N(24)–Ag(3)–N(31)	97.9(4)
Ag(4)–N(30)	2.193(9)	Ag(4)–N(19)	2.175(9)	N(13)–Ag(3)–N(31)	91.2(4)	N(15)–Ag(3)–N(31)	130.7(4)
Ag(4)–N(28)	2.558(9)	Ag(5)–N(18)	2.229(10)	N(19)–Ag(4)–N(30)	170.3(3)	N(19)–Ag(4)–N(28)	113.8(3)
Ag(5)–N(1)	2.156(8)	Ag(5)–N(16)	2.366(7)	N(30)–Ag(4)–N(28)	70.8(3)	N(1)–Ag(5)–N(18)	151.0(3)
Ag(6)–N(9)	2.469(8)	Ag(6)–N(7)	2.246(9)	N(1)–Ag(5)–N(16)	132.1(3)	N(18)–Ag(5)–N(16)	74.3(3)
Ag(6)–N(6)	2.172(8)	Ag(1)···Ag(5)	2.931(2)	N(6)–Ag(6)–N(7)	159.1(3)	N(6)–Ag(6)–N(9)	126.9(3)
Ag(1)···Ag(6)	3.046(2)	Ag(2)···Ag(4)	3.039(2)	N(7)–Ag(6)–N(9)	72.6(3)	Ag(5)···Ag(1)···Ag(6)	135.93(5)
Ag(2)···Ag(3)	2.921(1)	Ag(3)···Ag(5)	3.157(2)	Ag(2)···Ag(3)···Ag(5)	168.07(4)	Ag(2)···Ag(4)···Ag(6a)	158.94(4)
Ag(6)···Ag(4b)	3.343(2)	O(1w)···O(14)	2.819(8)	Ag(1)···Ag(5)···Ag(3)	154.76(4)	Ag(1)···Ag(6)···Ag(4b)	162.87(4)
O(1w)···O(17)	2.586(8)			Ag(3)···Ag(2)···Ag(4)	139.42(4)		
2							
Ag(1)–N(12)	2.227(5)	Ag(1)–N(10)	2.601(5)	N(12)–Ag(1)–N(6)	159.9(2)	N(12)–Ag(1)–N(4)	125.4(2)
Ag(1)–N(4)	2.359(5)	Ag(1)–N(6)	2.337(5)	N(6)–Ag(1)–N(4)	73.0(2)	N(12)–Ag(1)–N(10)	70.7(2)
Ag(2)–N(9)	2.216(5)	Ag(2)–N(1)	2.358(5)	N(6)–Ag(1)–N(10)	101.3(2)	N(4)–Ag(1)–N(10)	139.0(2)
Ag(2)–N(3)	2.316(5)	Ag(3)–N(16)	2.619(6)	N(9)–Ag(2)–N(1)	132.8(2)	N(9)–Ag(2)–N(3)	151.6(2)
Ag(3)–N(7)	2.148(6)	Ag(3)–N(18)	2.195(6)	N(3)–Ag(2)–N(1)	73.8(2)	N(18)–Ag(3)–N(16)	72.1(2)
Ag(4)–N(13)	2.615(6)	Ag(4)–N(15)	2.218(5)	N(7)–Ag(3)–N(16)	138.0(2)	N(7)–Ag(3)–N(18)	148.3(2)
Ag(1)···Ag(2)	2.9449(10)	Ag(1)···Ag(1a)	3.0290(12)	N(15b)–Ag(4)–N(13)	109.1(2)	N(15)–Ag(4)–N(13)	70.9(2)
Ag(2)···Ag(3)	2.9142(9)	Ag(3)···Ag(4)	2.9911(8)	Ag(2)···Ag(1)···Ag(1a)	155.76(3)	Ag(3)···Ag(2)···Ag(1)	137.24(3)
				Ag(2)···Ag(3)···Ag(4)	125.59(3)		
3							
Ag(1)–N(4)	2.286(5)	Ag(1)–N(6)	2.449(5)	N(4)–Ag(1)–N(10)	142.2(2)	N(4)–Ag(1)–N(12)	134.3(2)
Ag(1)–N(12)	2.367(5)	Ag(1)–N(10)	2.327(5)	N(10)–Ag(1)–N(12)	73.1(2)	N(4)–Ag(1)–N(6)	72.4(2)
Ag(2)–N(9)	2.274(5)	Ag(2)–N(3)	2.333(5)	N(10)–Ag(1)–N(6)	120.2(2)	N(12)–Ag(1)–N(6)	121.1(2)
Ag(2)–N(1)	2.329(5)	Ag(2)–N(7)	2.460(5)	N(9)–Ag(2)–N(1)	132.7(2)	N(9)–Ag(2)–N(3)	141.4(2)
Ag(3)–N(15)	2.303(5)	Ag(3)–N(19)	2.371(5)	N(1)–Ag(2)–N(3)	74.1(2)	N(9)–Ag(2)–N(7)	73.4(2)
Ag(3)–N(21)	2.303(5)	Ag(3)–N(13)	2.394(6)	N(1)–Ag(2)–N(7)	122.5(2)	N(3)–Ag(2)–N(7)	119.6(2)
Ag(4)–N(16)	2.299(5)	Ag(4)–N(18)	2.383(5)	N(15)–Ag(3)–N(21)	140.9(2)	N(15)–Ag(3)–N(19)	131.4(2)
Ag(4)–N(22)	2.326(5)	Ag(4)–N(24)	2.391(5)	N(21)–Ag(3)–N(19)	74.0(2)	N(15)–Ag(3)–N(13)	73.3(2)
Ag(5)–N(34)	2.299(5)	Ag(5)–N(27)	2.370(5)	N(21)–Ag(3)–N(13)	123.5(2)	N(19)–Ag(3)–N(13)	121.0(2)
Ag(5)–N(25)	2.331(6)	Ag(5)–N(36)	2.374(5)	N(16)–Ag(4)–N(22)	139.5(2)	N(16)–Ag(4)–N(18)	73.9(2)
Ag(6)–N(28)	2.318(5)	Ag(6)–N(30)	2.358(5)	N(22)–Ag(4)–N(18)	131.4(2)	N(16)–Ag(4)–N(24)	126.7(2)
Ag(6)–N(33)	2.356(5)	Ag(6)–N(31)	2.363(6)	N(22)–Ag(4)–N(24)	73.1(2)	N(18)–Ag(4)–N(24)	119.7(2)
Ag(1)···Ag(2)	3.3424(10)	O(2w)···O(4w)	2.705(5)	N(34)–Ag(5)–N(25)	132.0(2)	N(34)–Ag(5)–N(27)	136.3(2)
O(2w)···O(4w)	2.704(5)			N(25)–Ag(5)–N(27)	72.6(2)	N(34)–Ag(5)–N(36)	74.2(2)
				N(25)–Ag(5)–N(36)	125.7(2)	N(27)–Ag(5)–N(36)	125.1(2)
				N(28)–Ag(6)–N(33)	138.9(2)	N(28)–Ag(6)–N(30)	73.7(2)
				N(33)–Ag(6)–N(30)	130.2(2)	N(28)–Ag(6)–N(31)	129.1(2)
				N(33)–Ag(6)–N(31)	73.0(2)	N(30)–Ag(6)–N(31)	119.7(2)
4							
Ag(1)–N(4a)	2.310(5)	Ag(1)–N(4)	2.310(5)	N(4a)–Ag(1)–N(4)	136.0(2)	N(4a)–Ag(1)–N(3)	130.4(2)
Ag(1)–N(3)	2.426(5)	Ag(2)–N(1)	2.126(5)	N(4)–Ag(1)–N(3)	80.4(2)	N(3)–Ag(1)–N(3)	100.0(3)
Ag(2)–N(6)	2.123(5)	Ag(1)···Ag(2)	2.8307(7)	N(6)–Ag(2)–N(1)	176.8(2)	Ag(2)···Ag(1)···Ag(2a)	124.37(4)
Ag(2)···O(2)	2.960(6)						
5							
Ag(1)–N(6)	2.103(5)	Ag(1)–N(1)	2.126(6)	N(6)–Ag(1)–N(1)	175.4(2)	N(3)–Ag(2)–N(9)	153.1(2)
Ag(2)–N(9)	2.276(6)	Ag(2)–N(3)	2.205(6)	N(3)–Ag(2)–N(10)	125.1(2)	N(9)–Ag(2)–N(10)	81.5(2)
Ag(2)–N(10)	2.436(7)	Ag(3)–N(11)	2.215(6)	N(11)–Ag(3)–N(7)	145.9(2)	N(11)–Ag(3)–N(4b)	118.0(2)
Ag(3)–N(7)	2.341(6)	Ag(3)–(4b)	2.428(6)	N(7)–Ag(3)–N(4b)	94.7(2)	Ag(2)···Ag(1)···Ag(3a)	114.48(3)
Ag(1)···Ag(2)	2.9732(10)	Ag(1)···Ag(3a)	3.0643(10)	Ag(3)···Ag(2)···Ag(1)	149.86(3)	Ag(2)···Ag(3)···Ag(1b)	109.29(3)
Ag(2)···Ag(3)	2.8895(11)						

Symmetry codes: for **1**, a $x, -y + \frac{3}{2}, z - \frac{1}{2}$; b $x, -y + \frac{3}{2}, z + \frac{1}{2}$; for **2**, a $-x, y, -z + \frac{3}{2}$; b $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; for **4**, a $-x, y, -z + \frac{1}{2}$; for **5**, a $x, -y + \frac{1}{2}, z + \frac{1}{2}$; b $x, -y + \frac{1}{2}, z - \frac{1}{2}$.

distances are also well below the summed van der Waals radii of two silver atoms, indicating some weak metal–metal interaction. Similar to those in **1**, the bmimen ligands act in unusual fashions in co-ordination to the Ag atoms. One of the three crystallographically independent ligands acts in an unusual tetradentate bridging mode with a bidentate entity chelating Ag(1) and another bidentate entity bridging Ag(2) and Ag(3), as shown in Chart 1(c), which is different from those found in **1**. The other two bmimen ligands act in a bis(bidentate) bridging mode with each pair of bidentate entities chelating a Ag atom, similar to one of the co-ordination modes found in **1** (Chart 1(b)). The average bond distances of Ag–N$_{\mathrm{imidazole}}$ (2.314 Å) and Ag–N$_{\mathrm{imine}}$ (2.3875 Å) are slightly longer than those in **1**. Although not shown, the heptanuclear [Ag$_7$(bmimen)$_6$]$^{7+}$ cations in the solid are interconnected at each end by ligand-unsupported Ag···Ag interactions with the intermolecular Ag···Ag distance of 3.029(1) Å to form one-dimensional chains; such interaction is rarely observed,[3a,c,15,16] although a number of polymeric silver(I) complexes have been documented.[2c,e,f,7d–g,17] Adjacent imidazole rings in the helical chain are all aligned in a staggered fashion, no significant π–π stacking interaction is thus found in **2**.

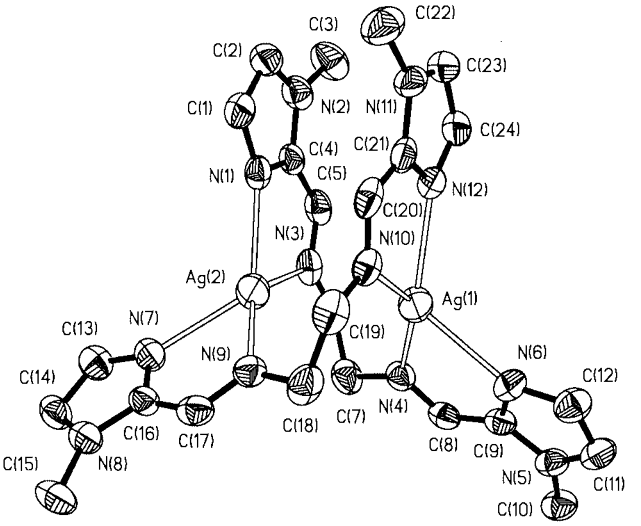

Fig. 3 An ORTEP[18] view of the double helicate in complex **3**.

As observed in complex **1**, some of the perchlorate oxygen atoms form weak contacts with the organic carbon atoms (3.1–3.3 Å). No significant metal–anion interaction has been found in **2**.

(c) $[Ag_2(bmimen)_2][NO_3]_2\cdot0.5H_2O$ 3. X-Ray diffraction shows that in the crystal structure of complex **3** there are three very similar but independent, discrete dinuclear $[Ag_2(bmimen)_2]^{2+}$ cations in an asymmetric unit with slightly different structural parameters. As shown in Fig. 3, each binuclear cation is a double helicate with an intramolecular Ag···Ag distance of 3.3424(10), 3.4460(10) or 3.6600(10) Å, respectively, in which each bidentate entity of bmimen chelates a Ag atom, resulting in an irregular four-co-ordination for each metal atom. The bis(bidentate) fashion of bmimen is similar to those found for **1** (see Chart 1(b)). The Ag–N distances (2.274(5)–2.460(5) Å) are also similar to those found for **1** and **2**. The helical structure is achieved by intramolecular twisting. It is worthy of note that most double helicates have been documented as copper(I) complexes; only a few examples of silver(I) complexes have been reported and most are generated by polypyridyl ligands.[2c,19] Silver(I) double helicates of di-Schiff bases are exemplified by $[Ag_2(bpen)_2][CF_3SO_3]_2$ (3.024 Å) [bpen = 1,2-bis(2-pyridylmethyleneamino)ethane].[2f] Finally, there is strong π–π stacking interaction between a pair of imidazole rings from different ligands in the double helicate, as shown in Fig. 3; the pair of imidazole rings are aligned in a slightly off-set fashion, being approximately parallel to each other with a dihedral angle of 3.4° and a face-to-face distance of 3.40 Å.

The nitrate ions have hydrogen bonds (O···O 2.5–2.7 Å) with the lattice water molecule, and some weak contacts, as observed in complex **1**, with the organic carbon atoms (3.15–3.3 Å). No significant metal–anion interaction has been found in **3**.

(d) $[Ag_3(bmimpn)_2][CF_3SO_3]_3$ 4. The crystal structure of complex **4** consists of discrete trinuclear $[Ag_3(bmimpn)_2]^{3+}$ cations and trifluoromethanesulfonate anions. As illustrated in Fig. 4, the cation possesses a twofold axis passing through Ag(1), and bmimpn acts in an unusual tetradentate mode to bridge Ag(1) and Ag(2) (see Chart 1(d)) with the diimine group chelating Ag(1) and the two imidazole groups simultaneously ligating Ag(2). The intramolecular Ag(1)···Ag(2) separation (2.8307(7) Å) indicates significant Ag···Ag interaction or week metal–metal bonding.[3a] In the cation, Ag(1) is four-co-ordinated by four nitrogen atoms from the imine groups of two bmimpn ligands, to form a distorted tetrahedron with the N–Ag(1)–N bond angles ranging from 80.4(2) to 136.0(2)° and the average Ag(1)–N bond distance is 2.368 Å. In contrast, Ag(2) atom is two-co-ordinated by two imidazole groups of a bmimpn ligand in a linear fashion with the N(1)–Ag(2)–N(6) bond angle 176.8(2)° and the average Ag(2)–N bond distance 2.125(6) Å. Similarly to that found in **3**, there is strong π–π stacking interaction between a pair of imidazole rings from different ligands in the helicate, as shown in Fig. 3; the pair of imidazole rings are aligned in a slightly off-set fashion, being approximately parallel to each other with a dihedral angle of 0.3° and a face-to-face distance of 3.41 Å.

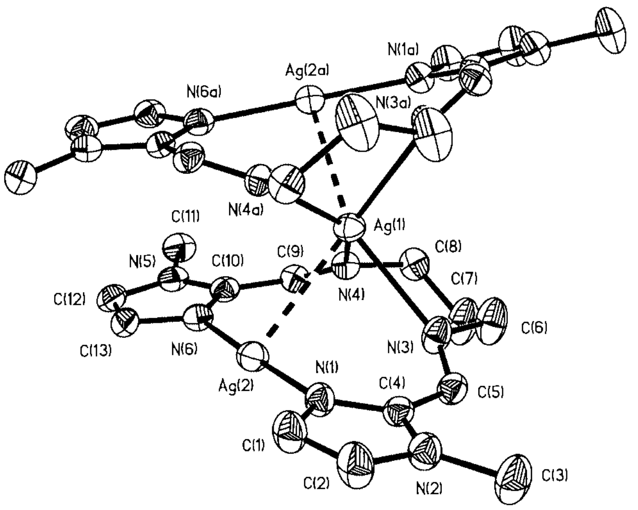

Fig. 4 An ORTEP view of the trinuclear cation in complex **4**. Symmetry code: a $-x, y, -z + \frac{1}{2}$.

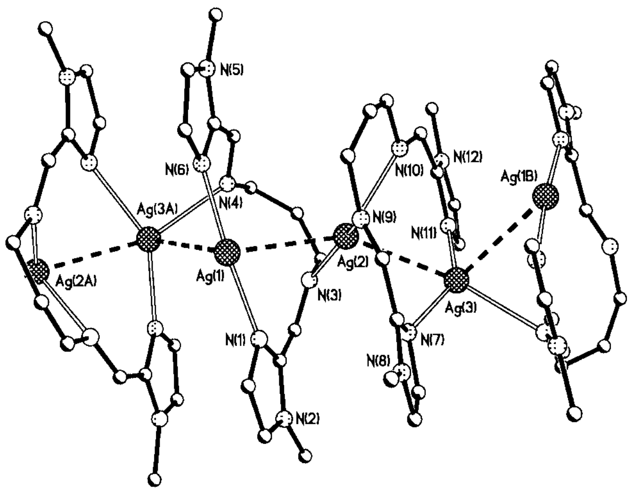

Fig. 5 Perspective view of the co-ordination environments in complex **5**.

The oxygen atoms of the anions have some weak contacts with the organic carbon atoms at 3.1–3.3 Å, while some weak metal–anion interaction with Ag···O distance at 2.96 Å is also found in complex **4**.

(e) $\{[Ag_3(bmimpn)_2]_n[NO_3]_{3n}\}$ 5. The crystal structure of complex **5** features polymeric helical $[Ag_3(bmimpn)_2]_n^{3n+}$ cations and nitrate anions. In the polymeric chain each structural unit consists of a trinuclear $[Ag_3(bmimpn)_2]$ core, as shown in Fig. 5. One of the two crystallographically independent ligands acts in an unusual tetradentate bridging fashion with the diimine group chelating Ag(2) and the two imidazole groups simultaneously ligating Ag(3), as shown in Chart 1(d); the other bmimpn acts in another unusual tetradentate bridging fashion with the two imidazole groups simultaneously ligating Ag(1) and two imine groups co-ordinated to Ag(2) and Ag(3a), respectively, as shown in Chart 1(e). Therefore the co-ordination geometry of Ag(1) is virtually linear with the N(6)–Ag(1)–N(1) bond angle at 175.4(2)°, whereas those of Ag(2) and Ag(3) are distorted Y-shaped with N–Ag–N bond angles in the range of 81.5(2) to 153.1(2)°. The metal atoms are arranged in a zigzag fashion with the Ag···Ag···Ag angles in the range of 109.29(3) to 149.86(3)° and are extended into helical infinite chains through the bridging co-ordinations, in which the adjacent Ag···Ag separations are in range of 2.8895(11) to 3.0643(10) Å. These intra-chain Ag···Ag distances are similar to those found for **1**–**4**, indicating weak metal–metal interaction. Detailed examination reveals the average bond distance of Ag–$N_{imidazole}$ (2.196 Å) is also shorter than that of Ag–N_{imine} (2.336 Å), in accordance with that in **4**. Adjacent imidazole rings in the infinite chain are arranged in a staggered fashion, exhibiting no significant π–π stacking interaction between the imidazole groups, similar to that found in **2**.

Similar to those found in complex **4**, the oxygen atoms of the anions have some weak contacts with the organic carbon atoms at 3.1–3.3 Å, while some weak metal–anion interactions with the Ag···O distance at 2.7 Å are also found.

Spectroscopy

The infrared spectra of complexes **1**, **2**, **3**, **4** and **5** show that the symmetric stretching vibration of C=N of the ligands is slightly sensitive to metal co-ordination and experiences an Einstein shift (to lower wavenumbers) of 6 to 14 cm^{-1}. The FAB mass spectra display peaks at *m*/*z* 316, 317, 351, 279 and 279 attributable to $[Ag_6(bmimen)_5(MeCN)]^{6+}$, $[Ag_7(bmimen)_6]^{7+}$, $[Ag_2(bmimen)_2]^{2+}$, $[Ag_3(bmimpn)_2]^{3+}$ and $[Ag_3(bmimpn)_2]^{3+}$, respectively, consistent with the crystal structures.

The ^1H NMR spectra of complexes **1**, **2** and **3**, being similar resonance patterns, show that the NCH_2 protons shift downfield while imine protons and imidazole ring protons undergo upfield shifts on complexation of the ligand with Ag^I. This behaviour causes a characteristic change of the sequence of the chemical shifts of the NCH_2, imine and imidazole ring protons as compared to those in the "free" ligand. The similarity in the ^1H NMR spectra of **1**, **2** and **3** indicates that these complexes have similar structures in solution although they have different structures in the solid. Based on the literature[2*f*,20] and the structure of **3** in the solid, it may be presumed that bmimen acts in a bis(bidentate) fashion (Chart 1(b)) in solution, and that in solution the structure of **3** retains the double helicate skeleton with a pair of homotopic bmimen ligands, while both **1** and **2** undergo deaggregation to generate dinuclear helicates structurally similar to that of **3** in solution.

Except for the upfield shift of the NCH_2 protons, the ^1H NMR spectra of complexes **4** and **5** show similar resonance patterns to those of **1**, **2** and **3**. The similarity suggests that bmimpn may function as a tetradentate ligand,[2*f*,20] whereas the upfield NCH_2 signals indicate that bmimen and bmimpn act in different ligation modes in solution, in accord with the solid structures. Possibly, the solid state structure of **4** is retained in solution, while **5** undergoes deaggregation to generate a trinuclear structure similar to that of **4** in solution.

Discussion

The bmimen and bmimpn ligands are obtained by condensation of 1,2-diaminoethane and 1,3-diaminopropane with 1-methylimidazole-2-carbaldehyde, respectively. The five oligomeric and polymeric silver(I) helicates with different metal : ligand ratios were obtained from equimolar mixtures of bmimen or bmimpn with $AgCF_3SO_3$, $AgClO_4$ and $AgNO_3$, respectively. The X-ray structural investigation confirms the different metal : ligand ratios of the complexes in the solid. The structural differences between **1**, **2** and **3**, as well as those of **4** and **5** in the solid, may apparently be attributed to the influence of the counter ions on crystallisation of the products as no significant interaction between the cations and anions has been found in the crystal structures. On the other hand, the structural differences between the bmimen (**1**, **2** and **3**) and bmimpn (**4** and **5**) complexes may be ascribed to the different backbones of the two ligands. With one more methylene group between the diimine group, the latter group of bmimpn in **4** and **5** can serve as a chelate entity in co-ordination to Ag^I, whereas the ethylenediimine group does not behave as a chelate entity in **1**, **2** and **3**. Our results also show the unusual flexibility of the di-Schiff bases in co-ordination to Ag^I, as demonstrated by the four unprecedented tridentate (Chart 1(a)) and tetradentate (Chart 1(b–e)) fashions featuring the imidazole-imine bidentate entity as a bridging group to ligate a pair of Ag atoms. In contrast, similar di-Schiff bases usually ligate a transition metal atom in a tetradentate chelate mode as shown in Chart 1(f).[3*a*,4,21] The similarity of the ^1H NMR spectra of the complexes with a particular ligand shows that they have the same structure in solution although they are different in the solid. This observation not only confirms the significant effect of the counter ions on the crystallisation process,[3*c*,*d*,14] but also demonstrates the flexibility of the ligands in their co-ordination, since the co-ordination modes may be changed in the crystallisation, or *vice versa*.

Conclusion

Self-assembly of two di-Schiff bases containing imidazole groups with silver(I) salts in a 1 : 1 metal : ligand ratio yielded five oligomeric and polymeric silver(I) helicates in different metal : ligand ratios, exhibiting four novel bridging modes of the di-Schiff bases in co-ordination to Ag atoms in the solid. The different aggregations and structures of the helicates in the solid are attributed to the influence of the counter ions in crystallisation and the different backbones of the organic ligands, in accord with the fact that the ^1H NMR spectra of the complexes with a particular ligand in solution are virtually identical.

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