Interaction of tripodal Schiff-base ligands with silver(I): structural and solution studies†

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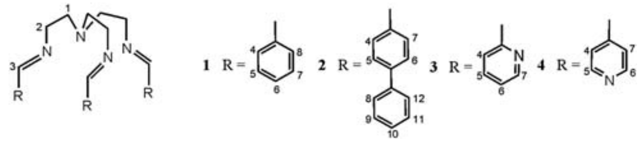
The binding and extraction of Ag(I) by tripodal Schiff-base ligands incorporating different aromatic podand arms are reported. These ligands have been synthesized by condensation of tris-(2-aminoethyl)amine with benzaldehyde (**1**), 4-phenylbenzaldehyde (**2**), 2- (**3**) and 4-pyridinecarbaldehyde (**4**). The structures of **1** and of four Ag(I) complexes [Ag(**1**)]ClO_4, [Ag(**2**)]ClO_4, $[Ag_3(\mathbf{3})_2](ClO_4)_3$ and $\{[Ag_3(\mathbf{4})_2](ClO_4)_3\}_n$ have been determined by single crystal X-ray diffraction. The structure of **1** shows intramolecular C–H$\cdots\pi$ (aromatic) interactions between phenyl rings, while bonding of Ag(I) *via* Ag–N interactions within the ionophore pocket is confirmed. In [Ag(**1**)]ClO_4, and [Ag(**2**)]ClO_4 additional long-range Ag–H interactions are observed, while π–π stacking occurs in the polynuclear species $[Ag_3(\mathbf{3})_2](ClO_4)_3$ and $\{[Ag_3(\mathbf{4})_2](ClO_4)_3\}_n$. Potentiometric titration, liquid–liquid extraction and ^{1}H NMR spectroscopic studies were performed to probe the nature of the silver complexes in solution. Potentiometric studies confirm increasing complex stability with Ag(I) in the order **2** < **4** < **1** < **3**, and enhanced Ag(I) extraction efficiency was observed with both increasing lipophilicity of the ionophore and the presence of additional donor groups. ^{1}H NMR spectroscopic studies were employed to probe the solution complexation behaviour of **1–4** towards Ag(I) and these confirm the formation of primarily 1 : 1 Ag : L complexes in solution.

Introduction

The complexation of Ag(I) in a range of supramolecular materials has received increasing attention, due to the coordinative flexibility of the d^{10} ion as well as to its well documented tendency to form strong complexes with nitrogen donor ligands.[1] Tripodal amine ligands based on tris(2-aminoethyl)amine (tren) are well known to interact with a range of transition and post transition metal ions[2] and typically complex metal ions within a well defined 'pocket'. For example, extending the structure of tren *via* Schiff-base condensation at each of the terminal amine groups by reaction with a range of aromatic aldehyde derivatives potentially offers a wide array of derivatives that can be matched to specific applications.[3,4] A structural study of the Schiff-base derivative **1** (Scheme 1), derived from tren and benzaldehyde confirmed the presence of a pocket in the solid state,[5] and complexation of Cu(I) with this ligand[6–9] confirms coordination of the metal ion by the four N-donor atoms with the phenyl substituents encapsulating the metal ion. This arrangement prevents further coordination to the metal centre on the exposed side[10] resulting in a tendency to form long-range intramolecular metal–hydrogen attractions.[6]



Scheme 1 Ligand structures for **1–4** with the labelling scheme used in the NMR investigations.

In contrast, the 2-pyridylmethyl substituted ligand **3** incorporates seven potential donors, and as described by Kirchner *et al.*[11] the presence of additional donors results in a variation of the coordination number from six for Fe(II), Ni(II), Cu(II) and Zn(II) (bridgehead tertiary nitrogen not coordinated) to pseudo-seven coordination for Co(II) and Mn(II) by "weak bonding" of the bridgehead amine. A subsequent study indicated the presence of similar pseudo-seven coordination in the corresponding Fe(II) complex.[12] Cr(III)[13] and Tc(II)[14] complexes of **3** have also been reported, with the smaller Cr(III) ion yielding a six-coordinate species,[13] while the larger Tc(II) ion shows a tendency for coordination of the apical tertiary amine.[14] More recent studies have expanded the range of complexes of **3** to include those of Cd(II)[15] and Ca(II).[16] The larger Ca(II) ion is coordinated to all seven N donor atoms,[16] while Cd(II) results in a six-coordinate species.[15]

To the best of our knowledge only one example of a Ag(I) tripodal Schiff-base complex of the above general type has been

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reported.[17] The Ag(I) ion in this 4-phenylnitrile substituted tripodal Schiff-base complex has a distorted coordination sphere in which Ag(I) is 5-coordinated to four nitrogens from the tripodal ligand and an acetonitrile molecule. The observed Ag–N bond lengths differ significantly, with distances ranging between 2.21 and 2.76 Å.[17] We report herein a comparative synthetic, solid-state and solution study of the interaction of Ag(I) with the tripodal Schiff-base ligands **1–4** (Scheme 1).

Experimental

Physical methods

All reagents and solvents were purchased from commercial sources and were used without further purification. NMR spectra were recorded on Bruker DPX300, DPX 500 or Jeol 300 MHz spectrometers; values are referenced to solvent or Me_4Si at 0 ppm in the case of the titrations. Electron Impact (EI) mass spectra were run on a Micromass Autospec mass spectrometer.

Ligand synthesis

The ligands were synthesized by slight modifications of literature methods.[7,17,18] Reaction of tris(2-aminoethyl)amine (tren) (0.94 g; 1 ml) with three equivalents of the corresponding aldehyde at 60 °C for 4 h was carried out under anhydrous conditions in dry methanol or ethanol (30 ml). The solvent was removed under reduce pressure to give the crude ligands. Ligand **1** was recrystallised from *n*-hexane/diethyl ether while **2** was recrystallised from chloroform/diethyl ether. Ligands **3** and **4** were obtained after any unreacted starting material was removed by vacuum distillation.

***N,N′,N″*-Tris(2-benzyliminoethyl)amine (1).** Yellowish solid; yield: 80%; $C_{27}H_{30}H_4$ (410.6), MS (EI) *m*/*z* 411 $[M + 1]^+$; ^1H NMR ($CDCl_3$) δ (ppm) 8.28 (s, 1H, CH), 7.49 (d, 2H, *ortho* C_6H_5), 7.31–7.39 (m, 3H, *meta* and *para* C_6H_5), 3.68 (t, 2H, CH_2), 2.93 (t, 2H, CH_2); ^{13}C NMR ($CDCl_3$) δ (ppm) 161.23, (CHN), 135.54, 129.74, 127.36 (C_6H_5), 59.43 (CH_2N), 55.00 (CH_2N).

Tris[2-(4′-phenylbenzyl)iminoethyl]amine (2). White solid, 98%, $C_{45}H_{42}N_4$ (638.9) MS (EI) *m*/*z* 639 $[M + 1]^+$; ^1H NMR ($CDCl_3$) δ (ppm) 8.14 (s, 1H, CH), 7.36–7.57 (m, 9H, ArH), 3.73 (t, 2H, CH_2), 2.94 (t, 2H, CH_2); ^{13}C NMR ($CDCl_3$) δ (ppm) 161.53 (CHN), 143.06, 140.34, 135.19, 128.84, 128.49, 127.68, 127.19, 127.07 ($C_{12}H_9$), 60.16 (CH_2N), 55.62 (CH_2N).

Tris[2-(2′-pyridylmethyl)iminoethyl]amine (3). Brown/yellow oil, 87%, $C_{24}H_{27}N_7$ (413.5) MS (EI) *m*/*z* 436 $[M + Na]^+$; ^1H NMR ($CDCl_3$) δ (ppm) 8.60 (m, 1H, C_5H_4N), 8.34 (s, 1H, CH), 7.90 (m, 1H, C_5H_4N), 7.70 (m, 1H, C_5H_4N), 7.28 (m, 1H, C_5H_4N), 3.77 (t, 2H, CH_2), 2.98 (t, 2H, CH_2); ^{13}C NMR ($CDCl_3$) δ (ppm) 162.72, (CHN), 154.46, 149.39, 136.50, 124.59, 122.25 (C_5H_4N), 59.87 (CH_2N), 55.27 (CH_2N).

Tris[2-(4-pyridylmethyl)iminoethyl]amine (4). Brown/yellow solid, 86%, $C_{24}H_{27}N_7$ (413.5) MS (EI) *m*/*z* 414 $[M + 1]^+$; ^1H NMR (DMSO) δ (ppm) 8.60 (q, 2H, C_5H_4N), 8.23 (s, 1H, CH), 7.49 (q, 2H, C_5H_4N), 3.66 (t, 2H, CH_2), 2.85 (t, 2H, CH_2); ^{13}C NMR ($CDCl_3$) δ (ppm) 160.19 (CHN), 150.83, 143.20, 122.12, (C_5H_5N), 60.57 (CH_2N), 55.59 (CH_2N).

Synthesis of the Ag(I) complexes

All reaction flasks were covered with aluminium foil to protect the Ag(I) species from light. For ligands **1**, **3** and **4** an equimolar amount of $AgClO_4$ in anhydrous methanol (5 ml) was added to the required ligand (0.5 mmol) in anhydrous methanol (10 ml) and the solution was stirred for 30 min at room temperature. Diethyl ether was added and the resulting precipitate collected by filtration was washed with methanol. The synthesis of the Ag(I) complex of the 4-biphenyl substituted ligand **2** was carried out in a similar manner except that a chloroform/methanol mixture was employed.

$[Ag(1)]ClO_4$. White solid, 87% yield, MS (EI) *m*/*z* 517; $C_{27}H_{30}AgN_4$ requires 517, ^1H NMR ($CDCl_3$) δ (ppm) 8.54 (s, CH, 1 H), 7.86 (d, *ortho* phenyl, 2 H), 7.46 (m, *para* phenyl, 2 H), 7.32 (m, *meta* phenyl, H), 3.77 (t, CH_2N, 2 H), 3.02 (t, NCH_2, 2 H). Anal. Calc. for $C_{27}H_{30}AgClN_4O_4$: C 52.49, H 4.89, N 9.07. Found: C 52.40, H 4.93, N 9.19%. Single crystals suitable for X-ray determination were grown by slow diffusion of diethyl ether into a dimethylformamide solution of the complex over one week in the dark.

$[Ag(2)]ClO_4$. White solid, 59% yield, MS (EI) *m*/*z* 745, $C_{45}H_{42}AgN_4$ requires 745, ^1H NMR (DMSO-d_6) δ (ppm) 8.68 (s, CH, 1 H), 8.00 (m, ArH, 2 H), 7.65 (m, ArH, 2 H), 7.58 (m, ArH, 2 H), 7.37 (m, ArH, 3 H), 3.86 (t, CH_2, 2 H), 3.03 (t, CH_2, 2 H). Anal. Calc. for $C_{45}H_{42}AgClN_4O_4$: C 63.80, H 5.00, N 6.62. Found: C 63.50, H 4.92, N 6.50%. Single crystals suitable for X-ray determination were grown by slow diffusion of diethyl ether into a dimethylformamide solution over one week in the dark.

$[Ag_3(3)_2](ClO_4)_3$. Yellow solid, 33% yield, MS (EI) *m*/*z* 520, $C_{24}H_{27}AgN_7$ requires 520, ^1H NMR (CD_3CN) δ (ppm) 8.49 (s, CH, 1 H), 8.44 (s, py, 1 H), 7.84 (t, py, 1 H), 7.72 (d, py, 1 H), 7.46 (t, py, 1 H), 3.79 (t, CH_2, 2 H), 2.95 (t, CH_2, 2 H). Anal. Calc. for $C_{48}H_{54}Ag_3Cl_3N_{14}O_{12}$: C 39.79, H 3.76, N 13.53. Found: C 40.13, H 3.78, N 13.60%. Single crystals suitable for X-ray determination were grown by slow diffusion of diethyl ether into a dimethylformamide solution of the complex over 3 weeks in the dark.

$\{[Ag_3(4)_2](ClO_4)_3\}_n$. White solid, 80% yield, MS (EI) *m*/*z* 520, $C_{24}H_{27}AgN_7$ requires 520, ^1H NMR (CD_3CN) δ (ppm) 8.53 (d, py and CH, 3 H), 7.56 (d, py, 2 H), 3.81 (t, CH_2, 2 H), 2.99 (t, CH_2, 2 H). Anal. Calc. for $C_{48}H_{54}Ag_3Cl_3N_{14}O_{12}\cdot 2H_2O$: C 38.82, H 3.94, N 13.20, found: C 38.72, H 3.75, N 12.91%. Single crystals suitable for X-ray determination were grown by slow diffusion of diethyl ether into a solution of the complex in MeCN over 3 weeks in the dark.

^1H NMR titration studies

^1H NMR titration experiments were carried out to investigate the formation of the Ag(I) complexes of **1–4**. The concentration of the ligand was 2 mM and defined aliquots of a 0.1 M $AgClO_4$ stock solution were added in each titration step. The ^1H NMR titrations of all ligands were carried out in a d_6-DMSO/d_3-MeCN 2 : 1 mixture.

Liquid–liquid extraction experiments

The liquid–liquid extraction experiments were performed at 23 ± 1 °C in microcentrifuge tubes (2 cm^3) undergoing mechanical shaking. The phase ratio $V_{(w)} : V_{(org)}$ (500 µl each) was 1 : 1, and an initial concentration for $AgClO_4$ of 1×10^{-4} M was used. Perchloric acid was added as counter ion at a concentration of 5×10^{-3} M. The ligand concentration in the organic phase was 1×10^{-3} M (except where variable concentration experiments were employed), and a mixing time of 30 min was used. All experiments were performed at a pH of 5.5 employing citric acid/NaOH buffer. The equilibrium pH was measured using an InLab micro pH electrode. After extraction, all samples were centrifuged and the phases separated. The distribution of metal ion concentrations was measured in both phases radiometrically by γ-radiation of ^{110m}Ag in a NaI (TI) scintillation counter (Cobra II/Canberra-Packard). In the solvent-extraction studies the distribution ratio, D_M, the quotient of the metal concentrations in the organic and aqueous phase, or the percentage extraction efficiency (E%) were obtained using: $D_M = c_{M(org)}/c_{M(w)}$ and $E[\%] = 100 \times D_M/(D_M + 1)$, respectively.

Potentiometric titrations

The potentiometric titrations experiments were carried out in duplicate in a 716 DMS Titrino (Methrom) titrator. Anhydrous silver nitrate (Merck) and tetraethylammonium perchlorate (Fluka) of the highest purity were used for all experiments. As solvent, anhydrous methanol (Merck; H_2O content less than 0.01%) was used. All stability constants were measured by means of an ion selective electrode for silver(I) (Methrom EA 282). During the titration the ionic strength is kept constant at $I = 0.05$ M using tetraethylammonium perchlorate as supporting electrolyte. A solution of a ligand (1×10^{-2} to 1×10^{-3} M) was added to a solution of $AgNO_3$ (1×10^{-3} to 1×10^{-4} M). Under these experimental conditions the activity coefficients are constant. From the measured potential E during the titrations the activity of the uncomplexed Ag(I) ion was calculated using the Nernst equation:

$$[\mathrm{Ag(I)}] = c_{Ag} \times 10^{\frac{(E-E_1)}{D}}$$

c_{Ag} is the total concentration of the silver ions and E_1 is the potential between the silver electrode and the reference electrode before the titration. The constant D at 25 °C is defined by $D = -2.303RT/nF = -59.16/n$ [mV] with the gas constant R, the temperature T, the Faraday constant F and the charge of the cation n. As reference, an identical solution of $AgNO_3$ together with a second silver electrode was used.

Crystallography†

The data for the crystal structures of **1**, [Ag(**1**)]ClO_4 and [Ag(**2**)]ClO_4 were collected on a STOE-IPDSII-diffractometer at 150 K (Mo-Kα) with STOE X-AREA.[19] SHELXS-97[20] was used for the structure solution and SHELXL-97[21] for the refinement. Absorption corrections were carried out empirically using X-RED,[22] X-SHAPE[21] and MULABS in PLATON.[23] Data for [Ag_3(**3**)$_2$](ClO_4)$_3$ and {[Ag_3(**4**)$_2$](ClO_4)$_3$}$_n$ were collected on a Bruker SMART1000 CCD area detector diffractometer at 150 K (Mo-Kα). Bruker SMART version 5.624[24] was used for the data collection with SIR92[25] and SHELXS-97[20] for the structure solution, and SHELXL-97[21] for refinement. Absorption corrections were carried out empirically using SADABS.[20]

Crystal and structure refinement data for all structures are summarised in Table 1. Where applicable, further details relating to the X-ray structure refinements are given in the ESI† along with tables of bond lengths and angles and selected H-bond and π-interaction geometries.

Table 1 Crystal data for ligand **1** and the Ag(I) complexes of **1–4**

Compound	**1**	[Ag(**1**)]ClO_4	[Ag(**2**)]ClO_4	[Ag_3(**3**)$_2$](ClO_4)$_3$	{[Ag_3(**4**)$_2$](ClO_4)$_3$}$_n$
Formula of refinement model	$C_{27}H_{30}N_4$	$C_{27}H_{30}AgClN_4O_4$	$C_{45}H_{42}AgClN_4O_4$	$C_{48}H_{54}Ag_3Cl_3N_{14}O_{12.5}$	$C_{48}H_{55}Ag_3Cl_3N_{14}O_{12.5}$
Crystal system	Monoclinic	Triclinic	Orthorhombic	Monoclinic	Triclinic
Space group	C2/c	$P\bar{1}$	$Pccn$	$I2$	$P\bar{1}$
a/Å	29.238(3)	10.6570(7)	18.0927(4)	21.150(2)	14.4780(9)
b/Å	9.5541(8)	11.2647(7)	29.2012(6)	12.4365(12)	14.9423(9)
c/Å	17.1115(15)	12.1892(7)	14.3480(4)	22.095(2)	15.0134(10)
α/°	90.00	108.952(5)	90.00	90.00	110.035(1)
β/°	99.104(7)	106.558(5)	90.00	105.399(2)	98.355(1)
γ/°	90.00	90.962(5)	90.00	90.00	92.026(1)
V/Å^3	4719.8(8)	1316.89(14)	7580.5(3)	5603.1(15)	3006.3(3)
D_c/g cm^{-3}	1.156	1.558	1.483	1.727	1.611
Z	8	2	8	4	2
Crystal size/mm	0.34 × 0.28 × 0.26	0.45 × 0.40 × 0.25	0.45 × 0.25 × 0.10	0.35 × 0.20 × 0.08	0.57 × 0.24 × 0.21
Crystal colour	Colourless	Colourless	Colourless	Yellow	Colourless
Crystal habit	Block	Block	Block	Tablet	Block
Temperature/K	150(2)	150(2)	150(2)	150(2)	150(2)
Reflections measured	21019	25 341	90 447	17 497	25 737
Unique reflections (R_{int})	4628 (0.067)	5582 (0.035)	8285 (0.064)	10 062 (0.047)	13 305 (0.016)
$R1(F)$, $wR2(F^2)$	0.0492, 0.1108	0.0187, 0.0487	0.0460, 0.1078	0.0405, 0.1100	0.0451, 0.1345
GoF	1.02	1.01	1.14	1.03	1.03
Residual density/e$^-$ Å^{-3}	−0.17, 0.17	−0.35, 0.52	−0.64, 2.49	−0.68, 1.18	−0.94, 1.69

Results and discussion

X-Ray structure of ligand 1

Crystals of the benzyl substituted ligand **1** suitable for X-ray structure analysis were grown from an *n*-hexane/diethyl ether mixture. Although the room temperature structure was reported in 2002,[5] it was re-determined as part of the present study at 150 K (Fig. 1) since it was of interest to re-examine the structure for the presence of potential intra- and inter-molecular interactions; this had not been carried out in the previous study. No significant intermolecular interactions were apparent within the structure. However, intramolecular CH–π (aromatic) interactions between the C–H of a phenyl group contacting the centre of a neighbouring aromatic ring (Fig. 1) are observed. The CH–π (centroid) distances lie between 2.65 and 2.75 Å with the C–H–centroid angles ranging between 136 and 138° (Table 2).[26] The presence of three CH–π (aromatic) interactions within **1** results in a cage-like arrangement, where the three podand arms are involved in CH–centroid interactions.

X-Ray structures of the Ag(I) complexes

Crystals of the Ag(I) complexes of **1–4** suitable for X-ray structure analysis were obtained by slow diffusion of diethyl ether into a solution of the respective complexes in dimethylformamide or acetonitrile.

The structure of [Ag(**1**)]ClO$_4$ (Fig. 2) confirms the metal centre to be four-coordinate with a distorted trigonal pyramidal geometry. The metal is bound to the tertiary bridgehead nitrogen donor N1 as well as to the three imine nitrogen donor atoms. The Ag(I) is located 0.53 Å out of trigonal plane defined by the three imine nitrogen atoms, away from the bridgehead N atom.

The Ag–N bond lengths to the imine nitrogen atoms (Ag1⋯N2 2.2948(13) Å, Ag1⋯N3 2.3138(12) Å, Ag1⋯N4 2.2946(13) Å) are significantly shorter than the Ag1–N1 distance (2.4554(12) Å). The rigidity of Schiff-base linkages and the positioning of the aromatic end groups appear to inhibit further coordination of solvent or anion groups to the Ag(I) centre. Ag–C$_{aryl}$ separations of 3.2760(17) to 3.3435(18) Å are observed between the Ag(I) centre and the centre of the aromatic rings, but these are outside the normal range (2.47–2.76 Å)[27] of significant Ag⋯π interactions. Interestingly however, three hydrogen atoms, one from each phenyl substituent, point towards the Ag(I) centre, corresponding to CH⋯Ag distances of 2.51–2.55 Å (Table 3); these are significantly shorter than the sum of the corresponding van der Waals radii (H 1.20 Å; Ag 1.72 Å).[28]

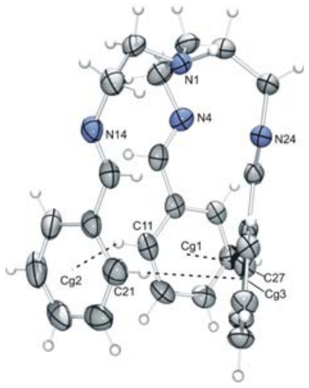

Fig. 1 X-Ray structure of **1**, selected atom labels and CH⋯π (centroid) interactions (dashed lines).

Table 2 CH⋯π (aromatic) interactions in **1** (Cg: ring centroid)

C–H	Cg	CH⋯Cg/Å	Cg/Å	C–H⋯Cg/°
C11–H11	Cg2	2.75	3.494(2)	136
C21–H21	Cg3	2.73	3.487(2)	138
C27–H27	Cg1	2.65	3.4226(18)	138

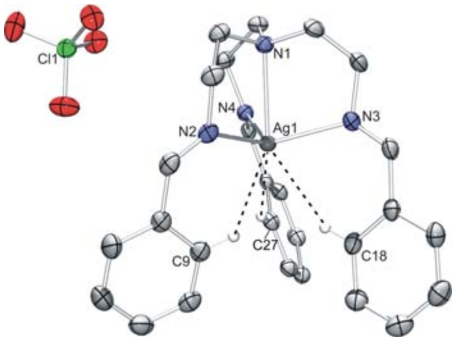

Fig. 2 ORTEP plot of [Ag(**1**)]ClO$_4$ with selected labeled atoms, 50% probability ellipsoids, non-interacting H-atoms omitted for clarity; CH⋯Ag interactions are shown as dashed lines.

Table 3 CH⋯Ag1 interactions in [Ag(**1**)]ClO$_4$

C–H	C–H/Å	H⋯Ag/Å
C9–H9A	0.95	2.54
C18–H18A	0.95	2.55
C27–H27A	0.95	2.51

It should be noted, that a similar placement of Cu(I) centres in two Cu(I) complexes of this ligand showing slightly longer metal–hydrogen distances have been described by Alyea *et al.*[6] and Brown *et al.*[9] Such C–H⋯metal contacts can perhaps be best described as weak hydrogen bonds.[29] Electron-rich transition metal ions have previously been proposed to act as such hydrogen bond acceptors.[30,31] The CH⋯Ag distances of 2.51–2.55 Å, the C–H–Ag angles of 135–141°[30] and the significant low-field shift (0.35 ppm) of the corresponding protons in the ^{1}H NMR spectrum studies (see below) are consistent with the presence Ag⋯H hydrogen-bonding interactions.[32]

In [Ag(**1**)]ClO$_4$ the cation and the counter anion are arranged in layers (Fig. S1, ESI†). A weak C25–H⋯O1 contact with the ClO$_4^-$ counter ion is observed with a separation of 3.192(7) Å (H⋯O 2.55 Å) and a C–H⋯O angle of 125° ($2 - x$, $1 - y$, $1 - z$ symmetry). The cationic [Ag(**1**)]$^+$ units are connected in a 2D plane by two weak intermolecular CH–π-aryl interactions with distances of 3.80 Å, from C11 to centroid Cg2 of the ring C22–C27 and from C23 to centroid Cg1 of the ring C4–C9 (Table S2, ESI†).

In order to increase the possibility of forming a pseudo-cage complex *via* intramolecular π–π or CH–π interactions involving the aromatic end groups, the Ag(I) complex of the analogous 4-biphenyl substituted ligand **2** was synthesised. The X-ray structure of [Ag(**2**)]ClO$_4$ is shown in Fig. 3.

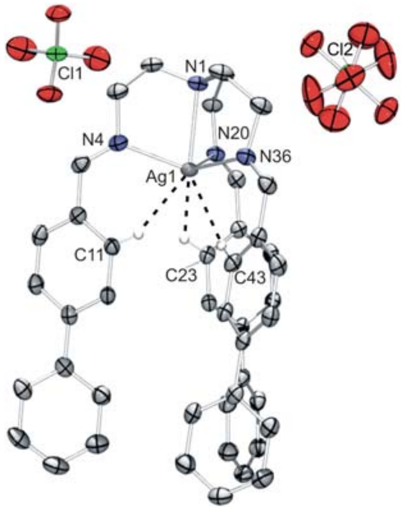

Fig. 3 ORTEP plot of [Ag(**2**)]ClO$_4$ with 50% probability ellipsoids; ClO$_4^-$ counter ion disordered over two positions with 50% occupancy, non-interacting H-atoms omitted for clarity; CH$\cdots$Ag interactions are shown as dashed lines.

The coordination geometry of the Ag(I) centre in [Ag(**2**)]ClO$_4$ is similar to that in [Ag(**1**)]ClO$_4$ and is pseudo-trigonal pyramidal involving coordination of the tertiary bridgehead nitrogen atom N1 and the three imine nitrogen atoms N4, N20 and N36. The Ag1–N1 bond (2.444(9) Å) is again significantly longer than the Ag–N$_{\text{imine}}$ bonds (Ag1$\cdots$N2 2.283(2) Å, Ag1$\cdots$N3 2.309(4) Å, Ag1$\cdots$N4 2.314(4) Å), with the Ag(I) ion located 0.53 Å out of the trigonal plane defined by the three imine N atoms, away from the bridgehead N atom. As in [Ag(**1**)]ClO$_4$ CH$\cdots$Ag interactions (C11H$\cdots$Ag1 2.51 Å, C23H$\cdots$Ag1 2.60 Å, C43H$\cdots$Ag1 2.44 Å) are observed in [Ag(**2**)]ClO$_4$. However, there is an increase in twist of the aromatic substituents away from the N1–Ag1 axis compared to [Ag(**1**)]ClO$_4$.

No intramolecular π–π or CH–π interactions between the biphenyl end groups are present in this complex. However, there is evidence for weak intermolecular CH–π interactions between ligand molecules (Fig. S2, ESI†) and CH$\cdots$O interactions involving the ClO$_4^-$ anion to form a 3D network throughout the lattice (Fig. S3 and Table S4 ESI†). The ClO$_4^-$ counter ion is disordered over two positions with 50% occupancy in each and occupies voids between columns of cations. One ClO$_4^-$ counter ion is disordered over two orientations of three of the O atoms.

The 2-pyridylmethyl substituents in **3** provide additional donor atoms resulting in the prospect of higher coordination numbers being generated if a 1 : 1 complex is formed. However, reaction of Ag(I) with **3** results in a 3 : 2 (M : L) complex [Ag$_3$(**3**)$_2$](ClO$_4$)$_3$ in the solid state (Fig. 4) in which the Ag(I) ion adopts trigonal pyramidal coordination *via* coordination to two imine and two pyridine nitrogen donor atoms. Two metal centres (Ag1 and Ag3) are bound to the imine nitrogen atoms and the pyridine nitrogen atoms of two podand arms from different ligand molecules. The third Ag(I) centre (Ag2) acts as a bridge between the above two complex units, being bound to the nitrogen donors of the remaining podand arms from each of the above ligand molecules. There is a slight difference in the coordination geometry of this Ag site; Ag2 is located 0.409 Å out of the plane formed by N7, N9 and N10 towards the fourth donor atom N6, whereas Ag1 and Ag3 are located 0.145 and 0.122 Å out of the planes formed by N2, N3 and N5 and N12, N13 and N14, respectively. There are no significant differences in the Ag–N bond lengths for (bridging) Ag2 relative to Ag1 and Ag3. In general, shorter bond lengths are observed for the Ag–N$_{\text{imine}}$ interactions (Ag–N$_{\text{imine}}$: 2.270(6) to 2.355(6) Å) than for the Ag–N$_{\text{py}}$ interactions (Ag–N$_{\text{py}}$: 2.345(6) to 2.481(6) Å), (Table S5 ESI†).

There is no evidence for intramolecular or intermolecular interactions between Ag(I) centres, with the internuclear separations Ag1 to Ag2 (3.47 Å) and Ag2 to Ag3 (3.54 Å) being greater than the van der Waals diameter for Ag (3.44 Å).[28]

The intra-centroid distances between pyridyl substituents lie between 3.577(4) and 3.851(5) Å with β-angles (angle between the ring normal of the aromatic ring plane and the centroid vector)[33] from 20 to 34° indicating the presence of long-range π–π stacking between the pyridine units. The ClO$_4^-$ counter ions and the solvate water molecules are located in layers beside the columns of face-to-face trinuclear Ag(I) complexes (see Fig. S4 ESI†). Two of the three ClO$_4^-$ ions are disordered. Numerous weak CH$\cdots$O interactions involving the ClO$_4^-$ counter ions are also present; these connect the trinuclear cation complexes along the crystallographic *a*- and *b*-axes (but not along the *c*-axis). The CH$\cdots$O distances lie between 2.38 and 2.51 Å (Table S6 ESI†).

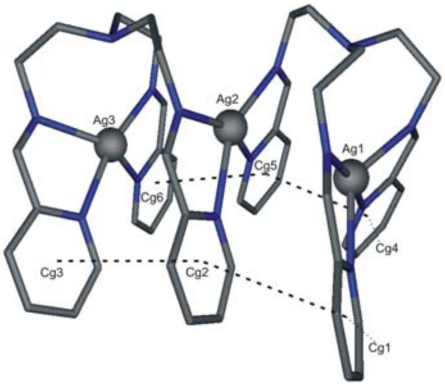

Fig. 4 The X-ray structure of [Ag$_3$(**3**)$_2$]ClO$_4$)$_3\cdot$0.5H$_2$O, H atoms, water and counter ions are omitted for clarity, selected intramolecular π–π interactions are shown (dashed lines).

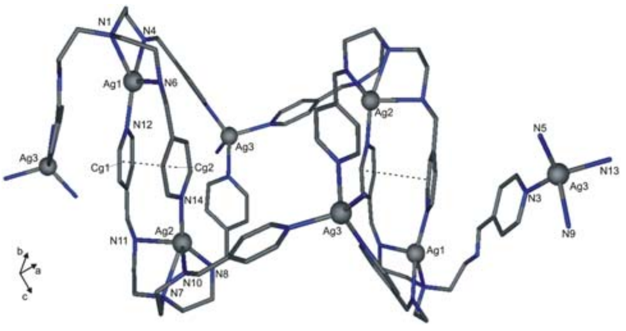

Fig. 5 The X-ray crystal structure of {[Ag$_3$(**4**)$_2$]ClO$_4$)$_3$}$_n$, dashed lines represent π–π interactions, H atoms and ClO$_4^-$ anions are omitted for clarity.

In **4** the pyridine nitrogen atoms are present in the 4-position of the aromatic substituents. Simultaneous coordination of the same Ag(I) ion to the pyridine donors as well as to the imine and amine nitrogen atoms positioned around the ligand bridgehead is thus sterically not possible. Reaction of this ligand with $AgClO_4$ affords the polymeric complex $\{[Ag_3(\mathbf{4})_2](ClO_4)_3\}_n$, the structure of which is shown in Fig. 5.

The Ag1 and Ag2 centres are not equivalent in $\{[Ag_3(\mathbf{4})_2](ClO_4)_3\}_n$; Ag1 has disordered tetrahedral coordination involving the bridgehead nitrogen atom N1 (Ag–N1 2.496(3) Å), the two imine nitrogen atoms N4 (Ag–N4 2.319(4) Å) and N6 (Ag–N6 2.477(4) Å) and the pyridyl nitrogen donor N12 (Ag–N12 2.242(3) Å). Ag2 is coordinated by the bridgehead nitrogen N7 (Ag–N7 2.540(5) Å), the imine nitrogen N8 (Ag–N8 2.281(4) Å) and the pyridyl nitrogen atom N14 (Ag–N14 2.238(4) Å). Further interactions with the imine nitrogen atoms N10 and N11 (Ag–N 2.675(4) and 2.607(4) Å, respectively) give Ag2 an overall five-coordinate distorted square-pyramidal geometry (τ = 0.43).[34] This difference in the coordination geometry between Ag1 and Ag2 is possibly in part a reflection of weak π–π stacking of the 'bridging' pyridine substituents. The centroid–centroid distance between the ring Cg1 (N12–C46) and the ring Cg2 (N14–C24) is 3.76 Å (angle β is 22°).[33]

Ag3 is coordinated to the 4-pyridine nitrogen donor atoms of four different ligand molecules to give a distorted tetrahedral geometry with bond lengths lying between 2.288(5) and 2.366(4) Å (Ag3–N3^{i} 2.288(5) Å, Ag3–N5 2.291(4) Å, Ag3–N9 2.366(4) Å, Ag3–N13^{ii} 2.323(4) Å; symmetry codes: (i) $-x, 1-y, 2-z$; (ii) $-x, -y, 1-z$). The N_{py}–Ag3–N_{py} angles lie between 98 and 121° (Table S7 ESI†).

The three ClO_4^- counter ions associated with each $[Ag_3(\mathbf{4})_2]^{3+}$ unit are disordered over four positions with occupancy of 1, 1, 0.5 and 0.5, respectively. Two of the anions, namely Cl2 and Cl4, are further disordered with 50% occupancy in each position. All anions are situated in the voids of the 1-D polymer formed by the complex cation and are involved in numerous short CH···O interactions. The CH···O distances lie between 2.23 and 2.52 Å (C···O distances between 3.108(8) and 3.470(5) Å). In addition, an intermolecular edge-to-face π–π interaction connects the polymeric chains. The separation between C9–H9A and the centroid of the ring N13–C48 (Cg3) is 3.836(5) Å (CH···Cg: 2.84 Å) and the X–H···π (centroid) angle is 173° (x, y, $1 + z$ symmetry). A schematic drawing of the weak interactions and a summary of the bond distances are given in Fig. S5 and Table S8 in the ESI.†

Stability constants for the Ag(I) complexes

Thermodynamic stability constants for the Ag(I) complexes of **1–4** in methanol were determined by the Ag(I) potentiometric titration technique (Table 4).

Table 4 Stability constants for the 1 : 1 (M : L) complexes of Ag(I) with **1–4** in MeOH. $[Ag]^+ = 1 \times 10^{-3}$ M, $[L] = 1 \times 10^{-3}$ M, $[Et_4NClO_4] = 5 \times 10^{-2}$ M; $T = 25$ °C

Ligand	**1**	**2**	**3**	**4**
$\log K_{[AgL]}$	9.10 ± 0.02	7.26 ± 0.03	12.95 ± 0.01	7.96 ± 0.04

The observed stabilities for the Ag(I) complexes of these tripodal ligands follow the order **2** < **4** < **1** < **3**. This order appears to reflect both the degree of steric hindrance of the N-donor sites within the tripodal pocket and the availability of the additional N-donor atoms for coordination to the Ag(I) centre. For example, the benzyl substituted ligand **1** gave a value of $\log K_{[AgL]} = 9.10$ while a significantly lower value of $\log K_{[AgL]} = 7.26$ was obtained for the 4′-phenylbenzyl substituted ligand **2**, possibly reflecting the presence of enhanced steric hindrance to coordination by the bulky biphenyl substituents in the latter case. For **3** the availability of additional pyridine N-donor atoms in the 2-position of the aromatic moiety results in a marked increase in the complex stability of approximately four orders of magnitude to $\log K_{[AgL]} = 12.95$. In **4** the pyridyl donor atoms are not correctly positioned for simultaneous binding to the same Ag(I) centre as the remaining ligand donors; consistent with this, the stability of the corresponding 1 : 1 Ag(I) complex was found to be significantly lower (Table 4).

^{1}H NMR titration

In order to investigate the complex stoichiometries in d_6-DMSO/d_3-MeCN (2 : 1 v/v) solution, ^{1}H NMR titrations of **1–4** with $AgClO_4$ were carried out. Fast NMR exchange was observed for all systems. As an example, representative spectra for **1** in the presence of increasing concentrations of $AgClO_4$ are shown in Fig. 6. The shifts of the proton signals on addition of Ag(I) are in agreement with interactions occurring between this metal ion and all of the N-donor atoms.

For each of **1–4**, the respective proton shifts were plotted against the molar ratio of Ag(I) (Fig. 7). In the case of **1** and **2**, the expected 1 : 1 complex formation was observed. Shifts in the signals for protons 1, 2 and 3 are in accord with the involvement of all four nitrogen donor atoms in complexation.

In the case of **3** significant shifts of the proton signals were observed up to a metal to ligand ratio of 3 : 2, in agreement with the stoichiometry observed in the X-ray structure of this

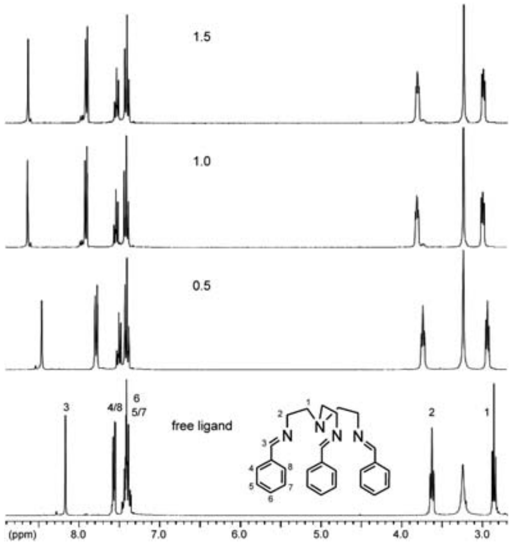

Fig. 6 ^{1}H NMR spectra of free ligand **1** and in the presence of molar increments of added $AgClO_4$ in d_6-DMSO/d_3-MeCN (2 : 1 v/v).

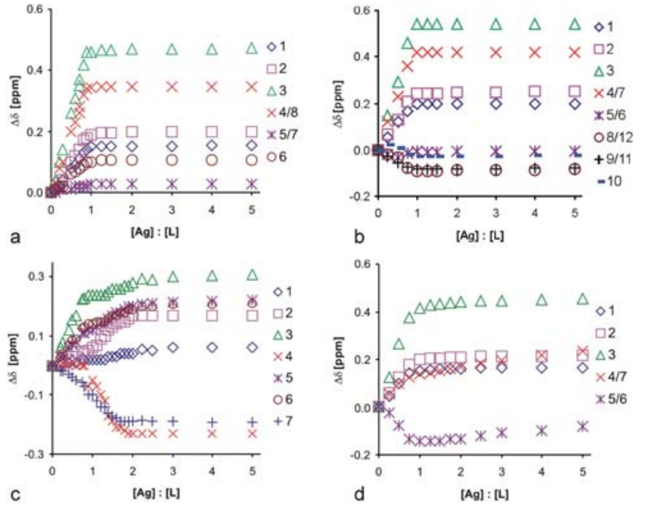

Fig. 7 Observed shifts in the proton signals of (a) **1**, (b) **2**, (c) **3** and (d) **4** in d_6-DMSO/d_3-MeCN (2 : 1 v/v) in the presence of increasing amounts of Ag(I) (for proton labels see Scheme 1).

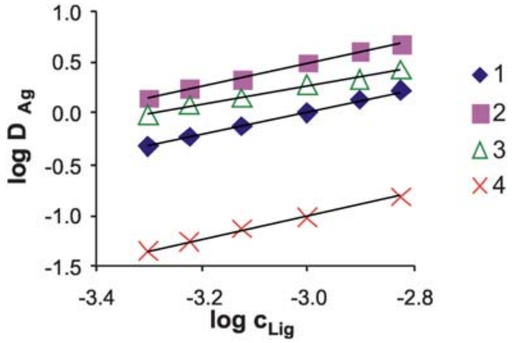

Fig. 8 Variable ligand concentration experiments for **1–4** with Ag(I) and perchlorate as the anion. $[AgClO_4] = 1 \times 10^{-4}$ M, $[HClO_4] = 5 \times 10^{-3}$ M; pH 5.5 (citric acid/NaOH buffer); [ligand] = 5×10^{-4} M – 1.5×10^{-3} M in $CHCl_3$; shaking time 30 min; $T = 23 \pm 1$ °C. Slopes: **1** $s = 1.14$; **2** $s = 1.14$; **3** $s = 0.9$; **4** $s = 1.14$.

complex. The shift of proton 1 is very small, ($\Delta\delta^{\mathrm{TM}} = 0.06$ ppm), suggesting no significant interaction of the tertiary bridgehead nitrogen with Ag(I) (as was also observed in the corresponding X-ray structure). Shifts of 0.2 to 0.4 ppm in all other proton signals are in accord with the expected interactions between the imine and pyridine nitrogens and Ag(I) being present.

The ^{1}H NMR titration of **4** with Ag(I) is in agreement with the formation of a 1 : 1 complex. All proton signals shift up to a 1 : 1 concentration ratio, with the shifts for protons 2 and 3 (Fig. 6) being the largest at $\Delta\delta^{\mathrm{TM}} = 0.25$ and 0.45 ppm respectively, as expected for the presence of strong interactions between the imine nitrogens and the Ag(I) ion. In this case the shift of the signal for proton 1 ($\Delta\delta^{\mathrm{TM}} = 0.17$ ppm) is in accord with the involvement of the bridgehead nitrogen in coordination to Ag(I).

Liquid–liquid extraction

The extraction behaviour of **1–4** toward Ag(I) was studied using the radiotracer technique.[35] An overview of the extraction results under comparable experimental conditions is given in Table 5. Under the conditions employed, the phenyl substituted derivative **1** showed an extraction efficiency of 50%, while for 4′-phenylbenzyl substituted ligand **2** the value was 76%. The presence of larger aromatic end-groups in **2** will result in an enhancement of the lipophilic properties of this ligand which, as observed, is expected to be reflected by higher extraction efficiency than for **1** (even through the thermodynamic stability of the 1 : 1 Ag(I) complex of **2** is in fact lower – see above).

Use of the 2-pyridyl substituted derivative **3** resulted in 66% extraction of Ag(I), whereas for the 4-pyridine derivative **4** the extraction was only 9%. As anticipated, the Ag(I) extraction obtained for **3** (66%) is also higher than obtained for **1** (50%). As mentioned earlier, in **4** the pyridine nitrogen atoms can not be aligned in a similar manner to those in **3** and hence are only available for intermolecular coordination. Further, the likely presence of 'free' polar pyridine groups in the case of **4** would be expected to induce enhanced water solubility, especially under acidic conditions, and result in increased bleeding of this ligand into the water phase and, if present, such behaviour may contribute to the dramatic decrease in Ag(I) extraction observed for this system.

Table 5 Percent Ag(I) extraction by **1–4**. $[AgClO_4] = 1 \times 10^{-4}$ M, $[HClO_4] = 5 \times 10^{-3}$ M; pH 5.5 (citric acid/NaOH buffer); [ligand] = 1×10^{-3} M in $CHCl_3$; shaking time 30 min; $T = 23 \pm 1$ °C

Ligand	1	2	3	4
% Ag(I) extraction	50	76	66	9

In order to probe the stoichiometries of the extracted species, extraction experiments were performed over a range of ligand concentration while the metal ion concentration was maintained at 1×10^{-4} M and the anion concentration was effectively constant. The value of $\log D_{Ag}$ ($D_{Ag} = c_{Ag(org)}/c_{Ag(w)}$) was plotted against $\log(c_{lig})$ (c_{lig} = ligand concentration) (Fig. 8). Provided a relatively simple equilibrium is involved, the slope of this plot gives the stoichiometry of the extracted species directly.[4,35]

The results show linear relationships between the logarithm of the distribution ratio (D_{Ag}) and the $\log(c_{lig})$ at pH 5.5 (Fig. 8) with slopes between 0.9 and 1.1 obtained for all four ligands consistent with the formation of 1 : 1 (Ag : L) species in chloroform under the conditions employed. Thus, the formation of 3 : 2 M : L complexes $[Ag_3(\mathbf{3})_2](ClO_4)_3$ and $\{[Ag_3(\mathbf{4})_2](ClO_4)_3\}_n$ reflects the isolated solid-state structures rather than the 1 : 1 complexes that, as for **1** and **2**, exist in solution.

Conclusions

The binding of Ag(I) to a series of tripodal Schiff-base ligands based on tren scaffolds has been investigated in both the solid-state and solution. These ligands show different Ag(I) coordination behaviour that in part reflects the number of available donor atoms as well as steric effects arising from the appended terminal aromatic groups. The incorporation of additional nitrogen donors in ligands **3** and **4** leads to the formation of both discrete trinuclear and polymeric solid-state complexes, respectively. In solution, structure/function relationships underlying the interaction of these species with Ag(I) have been probed employing potentiometric stability constant determinations, ^{1}H

NMR titration studies and liquid–liquid extraction experiments. The results indicate that the solution behaviour, while resembling the solid-state behaviour to some degree, tends to be more diverse, being clearly solvent dependent in particular instances.

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