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Highly pyramidalised heteroaromatic nitrogens in discrete multinuclear silver(I) complexes assembled from bis- and tris-(diallylamino)azines†

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2,4-Bis(diallylamino)-6-chloro-1,3,5-triazine reacts with silver(I) perchlorate and triflate to form discrete M_4L_2 assemblies in which the ligand uses all seven available (allyl and triazine) donors. 2,4,6-Tris(diallylamino)pyrimidine forms a discrete M_2L complex with silver triflate, in which the ligand is hypodentate. 2,4,6-Tris(diallylamino)-1,3,5-triazine forms a 1-D coordination polymer with silver perchlorate using seven donor groups, but employs all nine donors to form a discrete M_3L complex with silver triflate. In all these structures the nitrogen donors show unusually high levels of pyramidalisation.

Introduction

Silver(I) has proved to be a particularly useful metal for the self-assembly of a diverse range of metallosupramolecular species.[1–6] For some time we have used this metal for coordination to various nitrogen heterocyclic ligands for the assembly of both discrete and polymeric structures with diverse molecular architectures.[7–11] More recently, we[12–14] and others,[15–23] have shown that coordination of silver(I) to alkenes is a useful synthon in metallosupramolecular chemistry. In the accompanying paper[24] we combined these two approaches and showed that ligands containing a diallylamino group attached to a nitrogen heterocycle consistently lead to 1-D coordination polymers with coordination by the heterocyclic nitrogen and the allyl arms of the ligand. We now extend this approach to ligands containing two or three diallylamino groups attached to highly electron deficient heterocycles, which leads to (mainly) discrete assemblies in which the ligands gather together multiple silver atoms. A feature of these structures is the coordination of heterocyclic nitrogens with unusually highly pyramidalised geometries.

Results and discussion

The structures and syntheses of the ligands employed in this study are shown in Fig. 1. Reaction of cyanuric chloride with two equivalents of diallylamine gave the four armed ligand (**1**) in 72% yield. Alkylation of 2,4,6-triaminopyrimidine with allyl bromide gave ligand (**2**) in 97% yield. Reaction of cyanuric chloride with three equivalents of diallylamine furnished the symmetrical six armed ligand (**3**), albeit in only 28% yield. The ligands were isolated as yellow oily liquids after column chromatography on silica gel and were characterised by ^{1}H and ^{13}C NMR, infrared spectroscopy and mass spectrometry. Both the ^{1}H and ^{13}C NMR spectra of ligand (**1**) were more complicated than expected as the two allyl groups on each diallylamino group are non-equivalent due to restricted rotation about the N–triazine bond. Such a phenomenon has previously been noted in other dialkylamino triazines.[25]

Reaction of ligand (**1**) with two equivalents of silver(I) perchlorate and triflate gave crystalline complexes (**4**) and (**5**) in 15% and 78% yields, respectively. Complex (**4**), $[Ag_4(\mathbf{1})_2](ClO_4)_4$, crystallises in the triclinic space group $P\bar{1}$. The asymmetric unit contains one full molecule of (**1**), two silver atoms, a coordinated water molecule, a non-coordinated acetone molecule and two non-coordinated perchlorate counterions. The structure exists as a discrete tetranuclear (M_4L_2) assembly at the centre of which lies a crystallographic centre of inversion, as shown in Fig. 2. This involves the coordination of two ligand molecules with four silver atoms using all of the allyl arms and the three triazine ring nitrogen atoms.

The two crystallographically independent silver atoms are each four-coordinate, with τ_4 values[26] of 0.71 and 0.79 for Ag1 and Ag2 respectively, indicating seesaw geometries. Ag1 binds to two adjacent ligand molecules through the coordination of two allyl arms and two nitrogen atoms from triazine rings of adjacent ligands. In contrast, Ag2 is coordinated to two allyl arms of the same ligand, a nitrogen atom of the triazine ring and a water molecule. It is noteworthy that no two allyl arms from a single diallylamine

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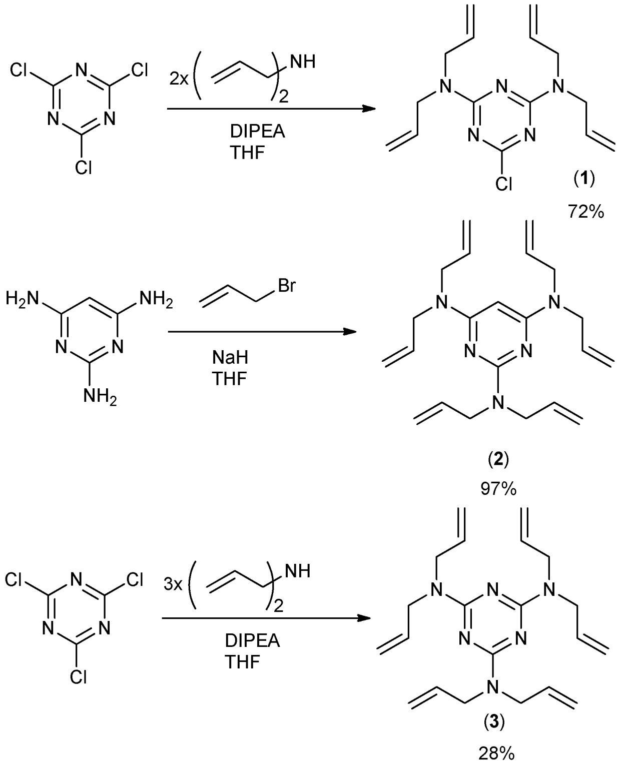


Fig. 1 Synthesis of the ligands employed in this study.

group coordinate with the same silver atom. The two independent silver atoms are separated by a distance of 6.620(1) Å, while symmetry related silvers are separated by 5.591(1) Å (Ag1) and 12.073(1) Å (Ag2).

Whereas the Ag–C bond distances (Table 1) fall in the normal range for silver alkene interactions,[12] the Ag–N bond distances are relatively long (2.408(1)–2.627(1) Å) but still shorter than those in previously reported silver complexes of related triazines.[18,27] However, an intriguing aspect of the structure is the unusually high pyramidalisation of the coordinated triazine nitrogens. In order to measure the extent of this distortion, we define the "pyramidalisation angle", α, as the angle subtended by the N–Ag vector to the plane of the ring, as shown in Fig. 3. This is determined from the distance (d) of the silver atom from the meanplane of the triazine ring and the N–Ag bond length (l), where sin (α) = d/l. An α angle of 0° would correspond to a trigonal planar sp^2 hybridised nitrogen, while a tetrahedral nitrogen would have an α angle of 54.75°. In the present case the α angles for N1, N2 and N3 are 42.2°, 51.7° and 35.0°, respectively, which represent unusually high degrees of pyramidalisation. Clearly the coordination of the silver to the nitrogen involves some contribution of the nitrogen p orbital, *i.e.* there is a rehybridisation of the sp^2 nitrogen towards sp^3. We believe that this is possible due to the low aromatic stabilisation energy of the highly electron deficient triazine ring, and is facilitated by the fact that the diallylamino nitrogen donates electron density into the triazine ring. This requires the exocyclic nitrogen p orbital to be coplanar with the ring which increases the steric environment at the ring nitrogens in the plane of the ring. Although unusual, such pyramidalisation does exist in some structures in the literature. For example, a silver complex of a bis(oxazolinyl)pyridine has a pyramidalised pyridine nitrogen with an α angle of 24°.[28]

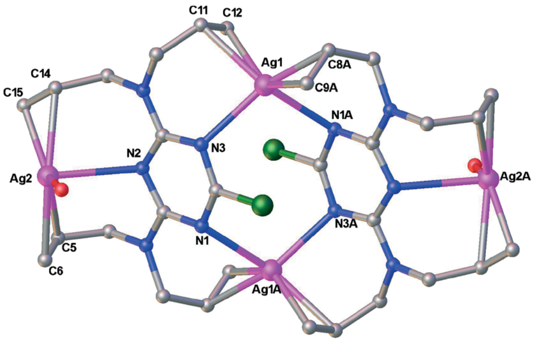


Fig. 2 The tetranuclear M_4L_2 discrete assembly of complex (**4**). All hydrogen atoms, the non-coordinated acetone molecule and the perchlorate counterions have been omitted for clarity.

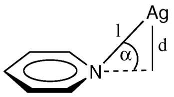


Fig. 3 Definition of the pyrimidalisation angle α.

Within this structure another feature of interest is the relative orientations of the two triazine rings, which positions the two chlorine atoms far from each other but close to the triazine ring of the other ligand. This arrangement results in mutual halogen–π interactions, with the distance between the centroid of the triazine ring and the chlorine atom being 3.259(5) Å, which represents a relatively strong interaction.[29] Finally, we note that the coordinated water molecule is hydrogen bonded to two non-coordinated perchlorate oxygen atoms.

Other weak intermolecular interactions are apparent in the crystal packing but play no obvious role in the self-assembly of this structure. Attempts to characterise this complex by mass spectrometry showed only ions from the uncomplexed ligand, indicating that this structure disassembles upon redisolving it in acetonitrile.

The analogous silver triflate complex (5), $[Ag_4(\mathbf{1})_2(OTf)_2](OTf)_2$, crystallises in the trigonal space group $R\bar{3}$, with one molecule of (1), two silver atoms, one coordinated and one non-coordinated triflate counterion in the asymmetric unit, all of which again assemble into a M_4L_2 structure (Fig. 4). Despite the very different space group and counterion, the structure is very similar to that of complex (4). The major difference is the replacement of the coordinated water molecule in complex (4) by a coordinated triflate anion in (5). A more subtle difference is the longer Ag2–N2 bond distance (Table 1), which presumably results from the greater steric demand of the coordinated triflate in (5), compared to the water molecule in (4). Other structural parameters are remarkably similar, including the pyramidalisation

Table 1 Selected bond lengths and angles. Note: CX,CY represents the midpoint of the bond between CX and CY

Complex (4)		Complex (5)		Complex (6)		Complex (7)		Complex (8)	
Ag1–C8A,C9A	2.311(3)	Ag1–N3A	2.414(4)	Ag1–N2	2.478(4)	Ag1–N3	2.486(4)	Ag1–C8,C9	2.308(4)
Ag1–N3	2.408(3)	Ag1–C8A,C9A	2.337(2)	Ag1–C6,C7	2.291(2)	Ag1–C8,C9	2.363(2)	Ag1–C17,C18	2.334(4)
Ag1–N1A	2.537(3)	Ag1–N1	2.445(4)	Ag1–C21,C22	2.283(2)	Ag1–C11,C12	2.331(2)	Ag1–N3	2.485(3)
Ag1–C11,C12	2.360(3)	Ag1–C11,C12	2.332(1)	Ag2–N1	2.482(4)	Ag1–C29,C30	2.359(2)	Ag2–C5,C6	2.281(4)
Ag2–O9	2.333(3)	Ag2–C5,C6	2.374(1)	Ag2–O3	2.391(2)	Ag2–N2	2.527(4)	Ag2–C11,C12	2.289(4)
Ag2–N2	2.627(3)	Ag2–C14,C15	2.373(2)	Ag2–C12,C13	2.287(2)	Ag2–C5,C6	2.300(1)	Ag2–N1	2.458(3)
Ag2–C5,C6	2.357(4)	Ag2–O2	2.410(4)	Ag2–C18,C19	2.335(2)	Ag2–O2	2.519(2)	Ag2–O2	2.407(3)
Ag2–C14,C15	2.306(4)	Ag2–N2	2.669(1)	Ag3–N6	2.530(4)	Ag2–C17,C18	2.313(1)	Ag3–O4	2.349(3)
				Ag3–O6	2.390(4)	Ag3–N7	2.500(4)	Ag3–N2	2.508(3)
				Ag3–C32,C33	2.334(2)	Ag3–C20,C21	2.373(2)	Ag3–C14,C15	2.331(4)
				Ag3–C38,C39	2.327(2)	Ag3–C35,C36	2.338(1)	Ag3–C20,C21	2.324(4)
				Ag4–N7	2.637(4)	Ag3–C41,C42	2.369(2)		
				Ag4–C29,C30	2.326(2)	Ag4–N8	2.628(4)		
				Ag4–C44,C45	2.327(2)	Ag4–C26,C27	2.296(1)		
				Ag4–O5	2.319(4)	Ag4–C38,C39	2.273(2)		
N3–Ag1–C11,C12	88.6(1)	N3A–Ag1–C8A,C9A	91.7(2)	N2–Ag1–C6,C7	91.2(1)	N3–Ag1–C8,C9	92.2(2)	N3–Ag1–C8,C9	92.7(1)
N3–Ag1–N1A	99.2(2)	N3A–Ag1–C11,C12	127.1(2)	N2–Ag1–C21,C22	95.4(2)	N3–Ag1–C11,C12	90.5(2)	N3–Ag1–C17,C18	90.8(2)
N3–Ag1–C8A,C9A	134.5(2)	N1–Ag1–C8A,C9A	128.5(1)	C6,C7–Ag1–C21,C22	136.1(2)	N3–Ag1–C29–C30	101.2(2)	C8,C9–Ag1–C17,C18	136.1(1)
C11,C12–Ag1–N1A	125.3(2)	C8A,C9A–Ag1–C11,C12	120.7(2)	N1–Ag2–O3	112.0(2)	C8,C9–Ag1–C11,C12	128.6(2)	N1–Ag2–O2	80.2(1)
C8A,C9A–Ag1–C11,C12	122.9(2)	N1–Ag1–C11,C12	89.5(2)	N1–Ag2–C12,C13	91.3(1)	C8,C9–Ag1–C29,C30	111.9(2)	N1–Ag2–C5,C6	95.5(2)
N1A–Ag1–C8A,C9A	88.5(1)	C5,C6–Ag2–C14,C15	150.4(2)	N1–Ag2–C18,C19	91.5(1)	C11,C12–Ag1–C29,C30	117.8(2)	N1–Ag2–C11,C12	91.2(2)
O9–Ag2–N2	91.4(1)	C5,C6–Ag2–O2	101.2(2)	O3–Ag2–C12,C13	123.1(3)	N2–Ag2–O2	77.7(2)	O2–Ag2–C5,C6	100.8(2)
O9–Ag2–C5,C6	111.1(2)	C14,C15–Ag2–O2	108.5(2)	O3–Ag2–C18,C19	100.7(3)	N2–Ag2–C5,C6	95.8(2)	O2–Ag2–C11,C12	118.3(2)
O9–Ag2–C14,C15	119.2(2)			C12,C13–Ag2–C18,C19	131.1(3)	N2–Ag2–C17,C18	89.8(2)	C5,C6–Ag2–C11,C12	140.8(2)
N2–Ag2–C5,C6	86.4(2)			N6–Ag3–O6	90.8(1)	O2–Ag2–C5,C6	113.6(3)	O4–Ag3–N2	94.4(1)
N2–Ag2–C14,C15	88.2(2)			N6–Ag3–C32,C33	89.1(2)	O2–Ag2–C17,C18	108.6(3)	O4–Ag3–C14,C15	116.7(2)
C5,C6–Ag2–C14,C15	129.6(2)			N6–Ag3–C38,C39	93.1(2)	C5,C6–Ag2–C17,C18	137.6(2)	O4–Ag3–C20,C21	112.2(2)
				O6–Ag3–C32,C33	119.7(2)	N7–Ag3–C20,C21	105.1(2)	N2–Ag3–C14,C15	89.7(2)
				O6–Ag3–C38,C39	107.0(2)	N7–Ag3–C35,C36	89.9(2)	N2–Ag3–C20,C21	90.7(2)
				C32,C33–Ag3–C38,C39	133.1(2)	N7–Ag3–C41,C42	91.1(2)	C14,C15–Ag3–C20,C21	130.9(2)
				N7–Ag4–O5	81.5(1)	C20,C21–Ag3–C41,C42	112.3(2)		
				N7–Ag4–C29,C30	85.9(2)	C20,C21–Ag3–C35,C36	119.0(2)		
				N7–Ag4–C44,C45	88.1(2)	C35,C36–Ag3–C41,C42	127.4(2)		
				O5–Ag4–C29,C30	119.3(2)	N8–Ag4–C26,C27	89.3(2)		
				O5–Ag4–C44,C45	110.2(2)	N8–Ag4–C38,C39	87.8(2)		
				C29,C30–Ag4–C44,C45	128.6(2)	C26,C27–Ag4–C38,C39	175.7(2)		

angles, the geometries of the silver atoms, the various distances between silver atoms separated by the bridging ligand (**1**) and the intramolecular halogen–π interactions.

Ligands (**2**) and (**3**) expand the number of allyl arms from four to six and differ not only in the symmetry of the ligand itself[7] but also in the number of available nitrogen donors from the central arene core. The complex (**6**), [Ag_2(**2**)OTf](OTf), of ligand (**2**) with silver(I) triflate crystallises in the monoclinic space group $P2_1/c$. The asymmetric unit contains two crystallographically independent assemblies (Fig. 5), each of which has one full molecule of (**2**), two silver atoms and a coordinated triflate counterion. There are also two non-coordinated triflate anions. The main difference between the two M_2L assemblies is in the manner in which the coordinated triflate anion

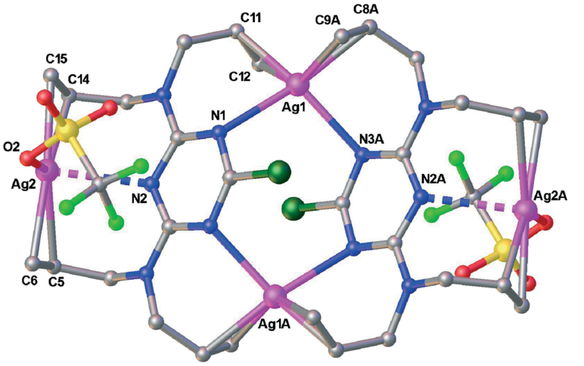


Fig. 4 The tetranuclear dimeric discrete assembly of complex (**5**). All hydrogen atoms and the non-coordinated triflate counterions have been omitted for clarity.

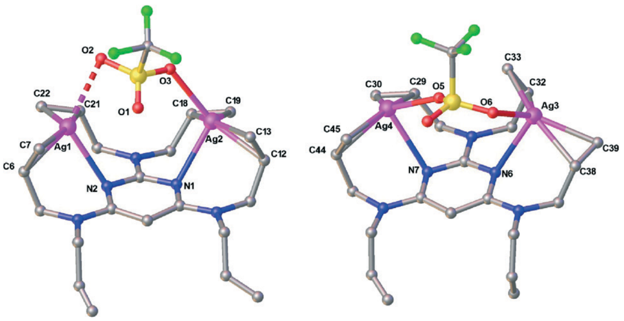


Fig. 5 The two independent units of complex (**6**). The non-coordinated triflate counterions and all hydrogen atoms have been omitted for clarity.

presents itself to the binuclear complex. Whilst the triflate anion is positioned in approximately the same position, in one case it is coordinated in a monodentate manner to just one of the silver atoms, with a very weak (2.642(2) Å) fourth interaction between Ag1 and O2, but in the other it has a bridging bidentate coordination mode. Thus three of the silvers are four-coordinate, while Ag1 is pseudo three-coordinate.

A notable feature of this structure is that in both assemblies ligand (2) is hypodentate,[30] with two of the six allyl arms remaining non-coordinated. Once again no two allyl arms from the same diallylamine group are chelated with a silver atom. Each molecule of (2) uses four allyl arms and the two pyrimidine nitrogens for coordination. The Ag–N bond distances (Table 1) are relatively long, ranging from 2.487(4) to 2.637(4) Å, with the shortest bond being to the pseudo three-coordinate silver. The pyrimidine ring nitrogens are again highly pyramidalised with α angles ranging between 47.6° and 55.3°.

The pseudo three-coordinate silver has a highly distorted trigonal planar geometry, while the four-coordinate silvers have seesaw geometries with τ_4 values of 0.75, 0.76 and 0.80 for Ag2, Ag3 and Ag4, respectively. The ligand bridges Ag1 and Ag2 with a separation of 4.976(1) Å; the corresponding separation of Ag3 and Ag4 is 5.147(1) Å. Thus ligand (2) acts by gathering together two silver atoms on the same face of the ligand and these are capped by a coordinated triflate anion.

Ligand (3) possesses six symmetry related allyl arms and three triazine nitrogens as potential donors. Reaction of this ligand with silver(I) perchlorate gave a complex (7), $[Ag_4(3)_2(ClO_4)]_n(ClO_4)_{3n}$, that crystallises in the orthorhombic space group $P2_12_12_1$, as a racemic twin. The asymmetric unit contains two molecules of (3), four silver atoms, one coordinated and three non-coordinated perchlorate anions (Fig. 6a). In this case the structure assembles into a helical 1-D coordination polymer that propagates along the *a* axis (Fig. 6b). Within the structure both molecules of (3) use five of their six allyl arms and two of the three ring nitrogens for coordination and are ambivergent,[31] acting in both a chelating and bridging mode.

The silver atoms are either coordinated with three allyl groups (Ag1 and Ag3) or with two (Ag2 and Ag4). No two allyl arms from the same diallylamine group chelate with a single silver atom, rather the coordinated allyl arms are either from adjacent diallylamine groups or adjacent ligands. Including the other (N and O) donors, Ag1, Ag2 and Ag3 are four-coordinate, while Ag4 is three-coordinate. The four-coordinate silvers have seesaw geometries with τ_4 values of 0.81, 0.77 and 0.81 for Ag1, Ag2 and Ag3, respectively, while the three-coordinate Ag4 atom has a T-shaped geometry (Table 1). Ag1 and Ag2 are bridged by the same ligand with a separation distance of 6.505(1) Å, while the corresponding distance between Ag3 and Ag4 is 6.664(1) Å. Ag2 and Ag3 are bridged by two allyl arms from the same diallylamine group with a separation distance of 7.947(1) Å.

Unlike the earlier examples, the silver atoms coordinate to the ring nitrogens on opposite faces of the ring. These nitrogens are again highly pyramidalised with α angles ranging between 40.6° and 48.6°. In this complex ligand (3) acts as a bridging ligand leading to a 1-D coordination polymer.

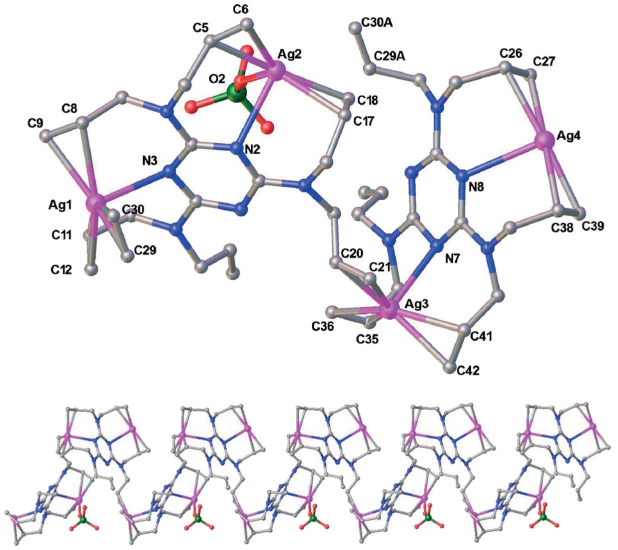


Fig. 6 (a) The asymmetric unit of complex (**7**) showing the labels of coordinated atoms. All hydrogen atoms and non-coordinated perchlorate anions are omitted for clarity (**8**). (b) A section of the 1-D polymer of (**7**).

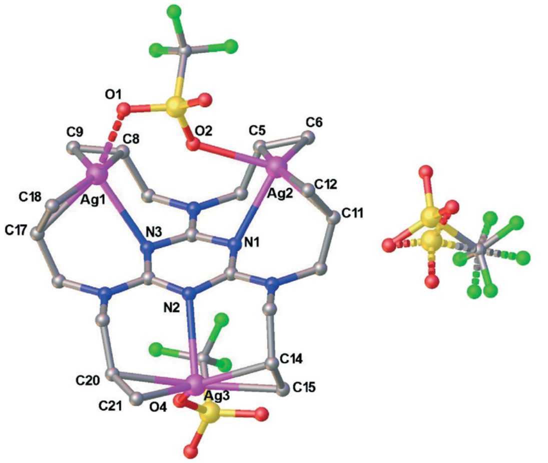


Fig. 7 The trinuclear discrete assembly of complex (**8**). All hydrogen atoms have been omitted for clarity.

However, the analogous complex (**8**), [Ag_3(**3**)$(OTf)_2$](OTf), prepared from silver triflate and (**3**) is once again a discrete species. Complex (**8**) crystallises in the monoclinic space group $P2_1/c$. The asymmetric unit contains one full molecule of (**3**), three silver atoms, two coordinated and one non-coordinated triflate counterion, as shown in Fig. 7. The non-coordinated triflate is disordered over two sites with 57% dominant position occupancy. Thus, this complex is a discrete M_3L species that uses all nine coordination sites available within the ligand.

The view shown in Fig. 7 serves to emphasise that the top half of this complex is remarkably similar to the M_2L complex (**6**) formed from the six armed pyrimidine ligand (**2**) in which two silver atoms are gathered together by four allyl arms on the same face of the ligand and two ring nitrogens, with capping by a coordinated triflate. However, in complex (**6**) the remaining two allyl arms remained uncoordinated on the opposite face of the ligand. In complex (**8**) these arms coordinate to a third silver (Ag3), facilitated by the presence of the extra nitrogen (N2) in the ring, which coordinates to this third silver.

The three silver atoms are four-coordinate with τ_4 values of 0.73, 0.72 and 0.80 for Ag1, Ag2 and Ag3, respectively. The triply bridging ligand separates silver atoms with the following distances: Ag1–Ag2 4.913 Å, Ag1–Ag3 6.529 Å and Ag2–Ag3 6.477 Å. Again the ring nitrogens are highly pyramidalised with α angles of 51.5°, 49.1° and 54.6° for N1, N2 and N3, respectively.

Experimental section

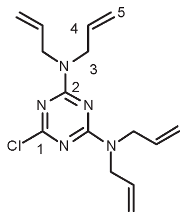
General

Unless otherwise specified, all reagents and starting materials were reagent grade, purchased from standard suppliers and used as received. Where anhydrous solvents were required, the HPLC-grade solvent was either distilled from standard drying agents or dried by passing over a sealed column of activated alumina. Melting points were recorded on an electrothermal melting point apparatus and are uncorrected. Elemental analyses were carried out by the Campbell Microanalytical Laboratory, University of Otago.

Infrared spectra were recorded on a Perkin-Elmer Spectrum One FTIR instrument operating in diffuse reflectance mode with samples prepared as KBr mulls (KBr), or in transmittance mode with liquid samples pressed between KBr discs (neat). NMR spectra were recorded on a Varian INOVA 500 or Varian Unity 300 instrument, operating at 500 and 300 MHz, respectively, for ^{1}H, and 125 and 75 MHz, respectively, for ^{13}C. Mass spectra were recorded on either a DIONEX Ultimate 3000 or Bruker MaXis 4G spectrometer, both of which were operated in high resolution positive ion electrospray mode. Samples were dissolved and diluted to the required concentration in HPLC grade acetonitrile or methanol.

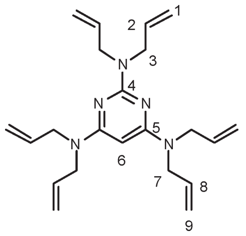
Preparation of ligands

Preparation of 2,4-bis(diallylamino)-6-chloro-1,3,5-triazine (1). A mixture of cyanuric chloride (1.84 g, 10 mmol) and *N*,*N*-diisopropylethylamine (DIPEA) (3.3 ml, 20 mmol) was stirred in dry THF (60 ml) at 0 °C. Diallylamine (2.5 ml, 20 mmol) was added to this solution and stirred for 2 hours at this temperature. The solution was then stirred at room temperature for 2 hours and then refluxed for 48 hours. The reaction was cooled to room temperature and the crystalline salt of DIPEA filtered off using a glass sintered filter funnel. Concentrating the filtrate *in vacuo* gave a brown oily liquid. Purification of the crude product with silica gel column chromatography using petroleum ether gave (**1**) as a light yellow oily liquid (2.20 g, 72%). ^{1}H N.M.R. (300MHz, $CDCl_3$): δ 4.10 (4H, d, J = 5.7 Hz, H3), 4.17 (4H, d, J = 5.7 Hz, H3), 5.10–5.17 (8H, m, H5), 5.72–5.85 (4H, m, H4). ^{13}C N.M.R. (75MHz, $CDCl_3$): δ 48.74, 48.85 C3, 117.33, 117.50 C5, 133.19, 133.57 C4, 165.06 C2, 169.73 C1. IR (cm^{-1}) 3080, 3010, 2924, 2855, 2526, 2326, 1850, 1642, 1563, 1494, 1414, 1314, 1254, 1237, 1195, 1171, 1110, 1044, 993, 969, 923, 850, 802, 737, 686. ESI-MS: found MNa$^+$ = 328.1307; $C_{15}H_{20}ClN_5Na$ requires MNa$^+$ = 328.1299.

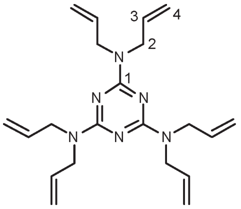


Preparation of 2,4,6-tris(diallylamino)pyrimidine (2). A mixture of 2,4,6-triaminopyrimidine (0.63 g, 5 mmol) and NaH (0.72 g, 30 mmol) was stirred in dry THF (50 ml) at 0 °C. Allyl bromide (2.61 ml, 30 mmol) was added dropwise to the mixture, which was then refluxed for a week. The reaction was cooled to room temperature and NaH was quenched with 30 ml of 1 M aqueous NH_4Cl solution. The organic layer was extracted with 3 × 30 ml of diethyl ether.

The ethereal extract was washed with water, brine and dried over $MgSO_4$. Evaporation under reduced pressure gave an impure yellow oily liquid. Purification of the crude product with silica gel column chromatography using 5 : 95 ethyl acetate : petroleum ether gave (2) as a light yellow oily liquid (1.78 g, 97%). ^{1}H N.M.R. (500MHz, $CDCl_3$): δ 4.01 (8H, d, J = 5.4 Hz, H7), 4.17 (4H, d, J = 6.0 Hz, H3), 4.94 (1H, s, H6), 5.06–5.16 (12H, m, H1,H9), 5.77–5.95 (6H, m, H2,H8). ^{13}C N.M.R. (126MHz, $CDCl_3$): δ 49.21 C3, 50.10 C7, 72.27 C6, 115.77 C1, 116.21 C9, 134.92 C8, 136.11 C2, 160.76 C4, 163.55 C5. IR (cm^{-1}) 3077, 3004, 2952, 2924, 2854, 1836, 1640, 1563, 1468, 1408, 1376, 1340, 1317, 1286, 1265, 1210, 1144, 1113, 994, 963, 916, 787. ESI-MS: found MH^+ = 366.2662; $C_{22}H_{32}N_5$ requires MH^+ = 366.2658.



Preparation of 2,4,6-tris(diallylamino)-1,3,5-triazine (3). A mixture of cyanuric chloride (0.922 g, 5 mmol) and *N*,*N*-diisopropylethylamine (DIPEA) (2.5 ml, 15 mmol) was stirred in dry THF (60 ml) at 0 °C. Diallylamine (1.8 ml, 15 mmol) was added to this solution and stirred for 2 hours at this temperature. The solution was then stirred at room temperature for 2 hours and then refluxed for 48 hours. The reaction was cooled to room temperature and the crystalline salt of DIPEA filtered off using a glass sintered filter funnel. Concentrating the filtrate *in vacuo* gave a brown oily liquid. Purification of the crude product with silica gel column chromatography using petroleum ether gave (3) as a light yellow oily liquid (0.518 g, 28%). ^{1}H N.M.R. (300MHz, $CDCl_3$): δ 4.13 (12H, d, J = 5.9 Hz, H2), 5.09 (6H, dd, J = 10.2, 1.6 Hz, H4), 5.15 (6H, dd, J = 17.1, 1.6 Hz, H4'), 5.78–5.91 (6H, m, H3). ^{13}C N.M.R. (126MHz, $CDCl_3$): δ 48.58 C2, 116.35 C4, 135.15 C3, 165.58 C1. IR (cm^{-1}) 3077, 2980, 2919, 1839, 1640, 1538, 1483, 1411, 1315, 1266, 1199, 995, 918, 808. ESI-MS: found MNa^+ = 389.2427; $C_{21}H_{30}N_6Na$ requires MNa^+ = 389.2424.



Preparation of complexes

Complexes (4) and (5). 2,4-Bis(diallylamino)-6-chloro-1,3,5-triazine (1) (0.0306 g, 0.1 mmol) dissolved in 1 ml acetone was added to a solution of silver(I) perchlorate (0.0415 g, 0.2 mmol) in acetone, which produced a white precipitate instantaneously. The precipitate was dissolved in a mixture of THF, water and

Table 2 X-ray experimental details

Complex	(4)	(5)	(6)	(7)	(8)
Empirical formula	$C_{18}H_{28}N_5O_{10}Cl_3Ag_2$	$C_{17}H_{20}N_5O_6F_6S_2ClAg_2$	$C_{24}H_{31}N_5O_6F_6S_2Ag_2$	$C_{21}H_{30}Ag_2Cl_2N_6O_8$	$C_{24}H_{30}N_6O_9F_9S_3Ag_3$
Formula weight	796.54	819.69	879.4	781.15	1137.33
Temperature/K	114	114(2)	112.15	117.15	114.15
Crystal system	Triclinic	Trigonal	Monoclinic	Orthorhombic	Monoclinic
Space group	$P\bar{1}$	$R\bar{3}$	$P2_1/c$	$P2_12_12_1$	$P2_1/c$
Unit cell dimensions: a/Å	10.9576(4)	41.519(6)	12.4040(4)	10.4069(2)	15.8670(7)
b/Å	12.0044(4)	41.519(6)	22.1684(8)	13.8557(4)	12.8111(5)
c/Å	12.1220(4)	9.1478(18)	23.4044(8)	37.5419(10)	18.0525(8)
α/°	65.317(2)	90	90	90	90
β/°	70.029(2)	90	97.655(2)	90	93.503(2)
γ/°	76.155(2)	120	90	90	90
Volume/Å^3	1352.96(8)	13657(4)	6378.3(4)	5413.4(2)	3662.7(3)
Z	2	18	8	8	4
Density (calculated) Mg m^{-3}	1.955	1.794	1.832	1.917	2.062
Absorption coefficient mm^{-1}	1.804	1.591	1.44	1.702	1.861
F(000)	792	7236	3504	3120	2232
Crystal size mm^{-3}	0.45 × 0.26 × 0.20	0.30 × 0.12 × 0.06	0.45 × 0.40 × 0.38	0.48 × 0.30 × 0.14	0.40 × 0.29 × 0.07
θ range for data collection (°)	5.16 to 50.1°	4.6 to 50.1°	3.32 to 51.44°	4.48 to 50.1°	4.52 to 50.1°
Reflections collected	25396	13776	127348	103327	68271
Independent reflections [R(int)]	4793[0.0474]	5354[0.0418]	12139[0.0564]	9594[0.0660]	6487[0.0825]
Completeness %	100	99.9	99.8	99.9	99.8
Data/restraints/parameters	4793/2/350	5354/0/352	12139/0/816	9594/0/703	6487/30/533
Goodness-of-fit on F^2	1.054	1.046	1.022	1.132	0.97
Final R_1 indices [$I > 2\sigma(I)$]	R_1 = 0.0313	R_1 = 0.0453	R_1 = 0.0474	R_1 = 0.0370	R_1 = 0.0320
	wR_2 = 0.0785	wR_2 = 0.1406	wR_2 = 0.1183	wR_2 = 0.0897	wR_2 = 0.0636
Final R indices [all data]	R_1 = 0.0408	R_1 = 0.0508	R_1 = 0.0656	R_1 = 0.041	R_1 = 0.0518
	wR_2 = 0.0817	wR_2 = 0.1463	wR_2 = 0.1307	wR_2 = 0.0919	wR_2 = 0.0681
Largest diff. peak/hole/e Å^{-3}	1.20/−0.90	1.93/−0.73	2.41/−1.80	2.44/−2.75	0.75/−0.61

acetone. Slow evaporation of the solvent over a period of time resulted in the isolation of colourless crystals of (4) suitable for single crystal X-ray structure analysis. Yield 0.0105 g, 15%. M.p. 259–261 °C (dec). IR (cm^{-1}) 3078, 3010, 2981, 2924, 1708, 1643, 1604, 1562, 1497, 1420, 1317, 1238, 1099, 970, 922, 841, 802, 627. Elem. anal. found: C, 25.89; H, 2.83; N, 9.22. Calc. for $C_{15}H_{20}N_5Cl.2AgClO_4 \cdot 1/2CH_3COCH_3 \cdot 1/2H_2O$: C, 26.13; H, 3.19; N, 9.23. Analogous reaction with silver triflate gave complex (5) in 56% yield. M.p. 128–130 °C. IR (cm^{-1}) 3701, 3079, 3010, 2982, 2924, 1718, 1642, 1608, 1560, 1539, 1497, 1424, 1341, 1282, 1252, 1235, 1174, 1103, 1032, 970, 947, 921, 852, 803, 656, 639, 574, 517.

Complex (6). 2,4,6-Tris(diallylamino)pyrimidine (2) (0.0366 g, 0.1 mmol) was dissolved in 1 ml dichloromethane and was added to a solution of silver(I) triflate (0.0771 g, 0.3 mmol) in 1 ml acetone. The solution was left in darkness at room temperature and diethyl ether was allowed to diffuse into the solution. This enabled the isolation of colourless crystals suitable for single crystal X-ray analysis. Yield 0.0495 g, 56%. M.p. 128–130 °C. IR (cm^{-1}) 3480, 3078, 2924, 2854, 1731, 1640, 1563, 1468, 1409, 1356, 1253, 1208, 1174, 1051, 993, 917, 850, 787, 767, 658, 637, 578, 521. Elem. anal. found: C, 35.01, H, 3.95; N, 7.67. Calc. for $C_{22}H_{31}N_5 \cdot 2AgSO_3CF_3 \cdot CH_3COCH_3$: C, 34.59; H, 3.98; N, 7.47.

Complex (7). 2,4,6-Tris(diallylamino)-1,3,5-triazine (3) (0.0635 g, 0.17 mmol) was dissolved in 1 ml acetone and was added to silver(I) perchlorate (0.1075 g, 0.52 mmol) also dissolved in 1 ml acetone. The solution was left in darkness at room temperature and diethyl ether was allowed to diffuse into the solution. This enabled the isolation of colourless crystals suitable for single crystal X-ray analysis. Yield 0.0789 g, 59%. M.p. 119–121 °C. IR (cm^{-1}) 3078, 3008, 2925, 1641, 1596, 1536, 1487, 1413, 1363, 1320, 1269, 1199, 1100, 940, 919, 837, 808, 660, 625. Elem. anal. found: C, 32.46; H, 3.76; N, 10.88. Calc. for $C_{21}H_{30}N_6 \cdot 2AgClO_4$: C, 32.29; H, 3.87; N, 10.76.

Complex (8). 2,4,6-Tris(diallylamino)-1,3,5-triazine (3) (0.0367 g, 0.1 mmol) was dissolved in 1 ml acetone and was added to silver(I) triflate (0.0771 g, 0.3 mmol) also dissolved in 1 ml acetone. The solution was left in darkness at room temperature and diethyl ether was allowed to diffuse into the solution. This led to the isolation of colourless crystals suitable for single crystal X-ray structure analysis. Yield 0.0752 g, 66%. M.p. 159–161 °C. IR (cm^{-1}) 3482, 3077, 3009, 2980, 2918, 1640, 1536, 1484, 1412, 1314, 1267, 1199, 1114, 1050, 995, 919, 860, 809, 767, 755, 658, 578, 520. Elem. anal. found: C, 25.75; H, 2.78; N, 7.61. Calc. for $C_{21}H_{30}N_6 \cdot 3AgSO_3CF_3$: C, 25.35; H, 2.66; N, 7.39.

Crystallography

X-Ray crystallographic data collection was carried out with a Bruker APEXII instrument, using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. All structures were solved using direct methods with SHELXS and refined on F^2 using all data by full matrix least-squares procedures with SHELXL.[32] Unless otherwise stated all non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.2 times the isotropic equivalent of their carrier atoms. Experimental details are listed in Table 2.

Conclusions

In this study we have shown that ligands containing two or three diallylamino groups attached to an azine (pyrimidine or triazine) unit are able to gather together multiple silver atoms using a combination of both the allyl arms and azine N donors. Bi-, tri-, tetra- and poly-nuclear complexes were formed, within which the silver atoms coordinate to highly pyramidalised azine nitrogens. We are not aware of other examples of silver(I) complexes of N-heterocyclic ligand that incorporate such pronounced degrees of pyramidalisation.

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