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Self-assembly of a novel pentanuclear centred-tetrahedral silver species

Edwin C. Constable,* Catherine E. Housecroft, Markus Neuburger, Sebastien Reymann and Sylvia Schaffner
Department of Chemistry, University of Basel, Spitalstrasse 51, CH 4056 Basel, Switzerland. E-mail: edwin.constable@unibas.ch

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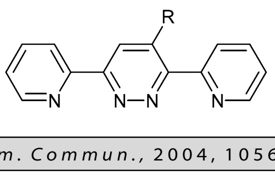
The reaction of 3,6-di(2-pyridyl)-4-trimethylsilylpyridazine with silver(I) tetrafluoroborate gives the pentanuclear complex cation [Ag$_5$L$_4$]$^{5+}$, in which the silver centres are arranged as a centred tetrahedron.

Metal-directed self-assembly is a powerful synthetic methodology for the bottom-up assembly of molecular machines and nanostructures.[1] Grid-like structures have attracted particular interest as molecular systems described as binary arrays that may be selectively addressed.[2] The majority of grids have been based upon structurally developed analogues of the prototype 3,6-di(2-pyridyl)pyridazine (dppz) ligand introduced by Osborn *et al*.[3] We have recently investigated the coordination behaviour of the structurally related ligand 3,6-di(2-pyridyl)-1,2,4,5-tetrazine[4,5] and of functionalised derivatives of dppz.[6] We found an unexpected, but persistent, trend for silver(I) to form planar complexes with ligands of this type, rather than the expected pseudotetrahedral species that would lead to grids.[5,6] In this paper, we report on the role of substituents in controlling the stoichiometry and structure of self-assembled silver(I) complexes of dppz ligands.

We have previously shown that dppz forms a planar [Ag(dppz)$_2$]$^+$ species in the solid state, whereas the phenyl-substituted derivative **2** gives a planar [Ag$_2$(**2**)$_2$]$^{2+}$ complex.[6] We considered that the introduction of bulky substituents on the 4-position of the pyridazine would force the adjacent 3-(2-pyridyl) ring significantly out of the plane, leading to a structure with a helical twist dividing the ligand into three metal-binding domains: a bidentate domain from the coplanar pyridine and pyridazine N1, and two monodentate domains from the pyridazine N2 and the out-of-plane pyridyl ring. Modelling (PM3, Spartan '04) of 3,6-di(2-pyridyl)-4-trimethylsilylpyridazine (**1**) indicated that the 3-(2-pyridyl) ring would form a torsion angle of ~ 25° with the pyridazine and we anticipated the formation of [Ag$_n$(**1**)$_n$]$^{n+}$ metallomacrocycles from the reaction of **1** with silver(I) salts. The new ligand **1** was prepared in 49% yield as a yellow powder from the Diels–Alder–retro-Diels–Alder reaction[7] of 3,6-di(2-pyridyl)tetrazine with trimethylsilylethyne in toluene (Scheme 1).†

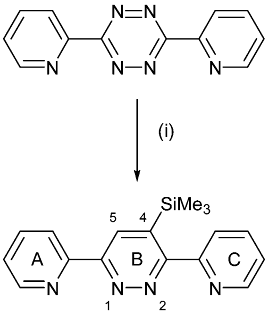
The reaction of **1** with silver tetrafluoroborate in acetonitrile in a 1:1 stoichiometry proceeded smoothly to give a yellow solution from which a yellow solid was obtained.‡ The ^{1}H NMR spectrum (298 K) of a solution of the recrystallised material in CD$_3$CN was sharp and well resolved and differed from that of **1** in the same solvent. Both the ^{1}H and ^{13}C NMR spectra showed a single ligand environment, although we have previously established[5,6] that with silver complexes of this type, the solution species are very often of a different stoichiometry to the solid-state materials.

The electrospray mass spectrum of an acetonitrile solution of the yellow crystalline material exhibited a base peak assigned to [Ag(**1**)$_2$]$^+$ and a major peak assigned to [Ag(**1**)(MeCN)]$^+$, reminiscent of the behaviour of dppz or **2**. However, in this case, a series of low intensity peaks corresponding to di-, tri-, tetra- and pentanuclear species were observed, leading us to suspect that a higher nuclearity metallocycle had been formed.



	R
dppz	H
1	SiMe$_3$
2	Ph

Crystals of the yellow complex obtained by the diffusion of diethyl ether vapour into an acetonitrile solution were suitable for X-ray analysis and were shown to have the stoichiometry [Ag$_5$(**1**)$_4$][BF$_4$]$_5$·3.5MeCN·(0.5MeCN:0.5C$_6$H$_{14}$)·H$_2$O.§ The cation is a structurally unique [Ag$_5$(**1**)$_4$]$^{5+}$ species which is best described as a tetrahedron of four silver atoms with a fifth silver at the centre (Fig. 1). The central silver Ag5 is in a distorted tetrahedral N$_4$ environment provided by the four pyridazine N2 donors [Ag5–N, 2.347(4)–2.364(4) Å; ∠N–Ag5–N, 88.64(15)–122.23(15)°]. Although the geometry is somewhat distorted, the sum of the six N–Ag–N angles is 659.56°, indicating that the best description is tetrahedral.[5,6] The remaining four silver centres each show one short bond to a nitrogen in a ring C [2.176(4)–2.219(4) Å; see Scheme 1 for nomenclature), one longer



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Scheme 1 *Reagents and conditions*: (i) Me$_3$SiC≡CH, toluene, 60 h, reflux, 49%.

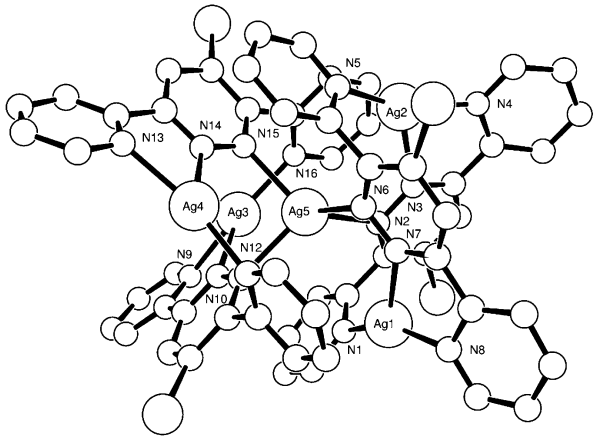

Fig. 1 The [Ag$_5$(**1**)$_4$]$^{5+}$ cation present in [Ag$_5$(**1**)$_4$][BF$_4$]$_5$·3.5MeCN·(0.5MeCN:0.5C$_6$H$_{14}$)·H$_2$O; hydrogen atoms and the methyl groups of the trimethylsilyl substituents have been omitted for clarity. Selected bond lengths: Ag1–N1 2.177(5), Ag1–N7 2.393(4), Ag1–N8 2.241(5), Ag2–N3 2.419(4), Ag2–N4 2.220(5), Ag2–N5 2.176(4), Ag3–N9 2.321(4), Ag3–N10 2.413(4), Ag3–N16 2.219(4), Ag3–N18 2.624(6), Ag4–N12 2.186(4), Ag4–N13 2.287(5), Ag4–N14 2.380(4), Ag5–N2 2.364(4), Ag5–N6 2.347(4), Ag5–N11 2.364(4), Ag5–N15 2.353(4) Å.

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bond to a nitrogen in a ring A [2.220(5)–2.321(4) Å] and longer contacts to a chelating N1 of a ring B [2.380(4)–2.419(4) Å], together with a contact to the fluorine of a tetrafluoroborate anion (Ag···F, 2.847–3.248 Å). The coordination geometry is best described as two-coordinate linear [N–Ag–N, 155.80(16)–157.55(19)° for the two shortest Ag–N bonds] with an additional interaction with the chelating B1 donor. Each ligand binds the central silver atom and then acts as a bidentate donor and a monodentate donor to two further silver atoms of the outer Ag_4 tetrahedron. The torsion angles between the B and C rings lie between 65.7 and 74.4°, indicating that the basic structural premise was correct. However, instead of simply forming a [4 + 4] metallomacrocycle, an additional silver atom is bound to account for the four uncoordinated N2 atoms of the B ring that would otherwise result. The relationship between the four ligands and the silver core is shown in Fig. 2.

The original concept of introducing the non-planarity into ligand **1** has been successful, with the division into sub-domains being achieved through torsion angles of 14.5–33.1° between rings B and C of the four ligands. Finally, we note that the four silicon atoms and five silver atoms describe a metal-centred pair of stellated tetrahedra (Fig. 3).[8]

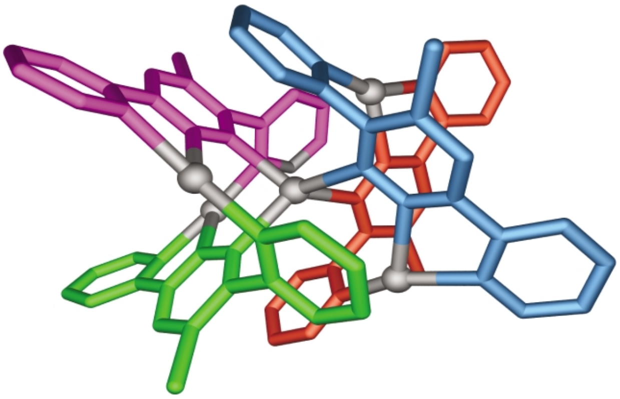

Fig. 2 A graphical representation of the cation $[Ag_5(\mathbf{1})_4]^{5+}$ emphasising the bridging nature of the ligands; hydrogen atoms and the methyl groups of the trimethylsilyl substituents have been omitted for clarity.

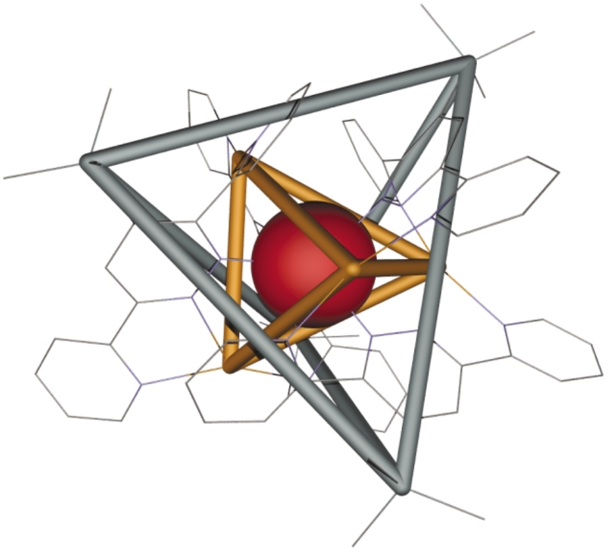

Fig. 3 The relationship between the two tetrahedra described by the four silicon atoms and the four outermost silver centres.

We are currently investigating the role of other sterically demanding substituents in the self-assembly of complexes with ligands of this type. We are also investigating the behaviour of **1** with other metal centres to probe whether the central silver(I) centre plays a templating role.

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Notes and references

† 3,6-Di(2-pyridyl)tetrazine (1 g, 4.24 mmol) and trimethylsilylethyne (0.528 g, 5.39 mmol) in toluene (50 mL) were refluxed for 60 h. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography [Al_2O_3, ethyl acetate–hexanes (1:2)] to give **1** as a yellow powder (0.640 g, 49%). Anal. calcd. for $C_{17}H_{18}N_4Si$ (%): C 66.63, H 5.92, N 18.28; found (%): C 66.99, H 5.96, N 18.24. ESI-MS: m/z $[Na(\mathbf{1})_2(CH_3CN)]^+$ 675 (100%). δ_H ($CDCl_3$, 500 MHz): 8.87 (s, 1H, H4B), 8.75 (ddd, *J* 4.8, 1.8, 0.9 Hz, 1H, H6A), 8.73 (dt, *J* 7.9, 1.0 Hz, 1H, H3A), 8.66 (ddd, *J* 4.8, 1.7, 0.9 Hz, 1H, H6C), 8.61 (dt, *J* 8.0, 1.0 Hz, 1H, H3C), 7.90 (td, *J* 8.1, 1.8 Hz, 1H, H4A), 7.88 (td, *J* 8.1, 1.8 Hz, 1H, H4C), 7.40 (ddd, *J* 7.5, 3.8, 1.2 Hz, 1H, H5A), 7.38 (ddd, *J* 7.5, 3.8, 1.2 Hz, 1H, H5C), 0.35 (s, 9H, $SiMe_3$).

‡ $AgBF_4$ (0.016 g, 0.08 mmol) and **1** (0.025 g, 0.08 mmol) were sonicated in acetonitrile (5 mL) for 5 min and then stirred under reflux a further 15 min. The solvent was evaporated and the yellow solid recrystallised from acetonitrile by slow diffusion of diethyl ether vapour to give yellow crystals (50%). ESI-MS: m/z $[Ag(\mathbf{1})(CH_3CN)]^+$ 454 (61%), $[Ag(\mathbf{1})_2]^+$ 719 (100%), $[Ag_2(\mathbf{1})_2(BF_4)]^+$ 914 (34%), $[Ag_3(\mathbf{1})_2(BF_4)_2]^+$ 1109 (7%), $[Ag_3(\mathbf{1})_3(BF_4)_2]^+$ 1416 (4%), $[Ag_4(\mathbf{1})_2(BF_4)_3]^+$ 1609 (6%), $[Ag_5(\mathbf{1})_3(BF_4)_4]^+$ 1804 (2%). δ_H (CD_3CN 500 MHz): 8.66 (ddd, *J* 4.3, 1.6, 0.9 Hz, 1H, H6A/H6C), 8.59 (ddd, *J* 4.8 Hz, 1.6 Hz, 0.8 Hz, 1H, H6C/H6A), 8.47 (s, 1H, H4B), 8.26 (d, *J* 8.0 Hz, 1H, H3A), 8.06 (td, *J* 7.8, 1.7Hz, 1H, H4A), 8.01 (dt, *J* 7.8, 1.9 Hz, 1H, H3C), 7.91 (td, *J* 7.7, 1.7 Hz, 1H, H4C), 7.61 (ddd, *J* 7.6, 4.9, 1.0 Hz, 1H, H5A/H5C), 7.53 (ddd, *J* 7.6, 4.9, 1.0 Hz, 1H, H5A/H5C), 0.19 (s, 9H, $SiMe_3$). Anal. calcd. for $C_{17}H_{18}N_4Si$ (%): C 66.63, H 5.92, N 18.28; found (%): C 66.99, H 5.96, N 18.24.

§ Crystal data for $[Ag_5(C_{17}H_{18}N_4Si)_4][BF_4]_5\cdot 0.5C_6H_{14}\cdot 3.5CH_3CN\cdot O(H_2)$: $C_{78}H_{89.5}Ag_5B_5F_{20}N_{19.5}O_1Si_4$, M = 2401.9, monoclinic, space group $P21/n$, a = 25.1896(3), b = 15.2357(2), c = 27.9532(3) Å, β = 106.6790(7)°, U = 10276.6 Å^3, Z = 4, D_c = 1.552 Mg m^{-3}, μ(Mo-K$_\alpha$) = 1.069 mm^{-1}, T = 173 K; 43 740 (23 151 independent) reflections collected on an Enraf Nonius Kappa CCD instrument. Refinement of 12 698 reflections (1315 parameters) with $I > 3.0\sigma(I)$ converged at final $R1$ = 0.0496, $wR2$ = 0.0510. One of the acetonitrile molecules and another solvent molecule were disordered; this was modelled with half-occupancy hexane and acetonitrile molecules. Only the oxygen atom of the fourfold-disordered water molecule was located. CCDC 231789. See http://www.rsc.org/suppdata/cc/b4/b402376e/ for crystallographic data in CIF or other electronic format.

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