Electronic supplementary information for

Control of molecular architecture by steric and electronic factors: dinuclear side-by-side *vs* tetranuclear [2x2] grid-type silver(I) complexes

*Jason R. Price,[a] Yanhua Lan,[a] Geoffrey B. Jameson[b] and Sally Brooker[a,]**

$[Ag_4(5)_4][BF_4]_4{\cdot}H_2O$: A solution of silver tetrafluoroborate (0.0125 g, 0.064 mmol) in nitromethane (5 mL) was added to a stirred yellow suspension of **5** (0.0224g, 0.064 mmol) in nitromethane (20 mL) causing an immediate colour change to blood red. The resulting solution was heated at reflux for 3 hrs, allowed to cool to room temperature and the volume reduced to ~1/3 under reduced pressure. Diethylether was diffused into the reaction solution yielding red needle-like crystals which, on drying *in vacuo*, gave $[Ag_4(\mathbf{5})_4][BF_4]_4{\cdot}H_2O$ (0.0261 g, 74 %). Found: C, 43.90; H, 3.44; N, 10.10. $C_{80}H_{72}N_{16}O_8B_4F_{16}Ag_4{\cdot}H_2O$ requires: C, 44.03; H, 3.42; N, 10.27.

$[Ag_2(6)_2][BF_4]_2$: As described for $[Ag_4(\mathbf{5})_4][BF_4]_4{\cdot}H_2O$. Red-orange needles (0.0223 g, 58%). Found: C, 50.88; H, 4.63; N, 9.96. $C_{48}H_{52}N_8B_2F_8Ag_2$ requires: C, 51.00; H, 4.64; N, 9.91.

Crystal data for $[C_2\text{-}Ag_4(\mathbf{5})_4]_4[S_4\text{-}Ag_4(\mathbf{5})_4][BF_4]_{20}$ (agg1t): $C_{100}H_{90}Ag_5B_4F_{16}N_{20}O_{10}$ (NB. molecular formula, M, F_{000}, D_c and μ are reported for only the crystallographically well defined part of the structure; see comments later), M = 2618.51, red block obtained by vapour diffusion of diethylether into a nitromethane solution, crystal dimensions 0.46 x 0.30 x 0.22 mm^3, tetragonal, I4(1)/a, a = 46.8568(4), b = 46.8568(4), c = 21.79970(10) Å, U = 47862.5(6) $Å^3$, μ = 0.888 mm^{-1}, Z = 16, D_c = 1.454 Mg/m^3, F(000) = 20944, T = 200 K. 145619 reflections were collected in the range $5.50° < 2\theta < 46.52°$. A semi-empirical absorption correction (SADABS) was applied (T_{max} = 0.85, T_{min} = 0.56). The 17147 independent reflections were used to solve the structure by direct methods (SHELXS-97).[14]

Five of the ten crystallographically independent methoxy groups, attached to the phenyl rings, are disordered with the methyl group occupying alternate sites with approximately equal occupancy. Disorder of two methoxyphenyl rings leads to bond angles at attached imino nitrogen atoms that deviate by up to 9° from expected values. One pair of disordered methoxyphenyl rings is inclined by 27.5°; the other pair is essentially coplanar, being inclined by 8.4°. Four of the five crystallographically independent tetrafluoroborate anions are well defined with the other showing substantial disorder. The latter tetrafluoroborate anion and the solvate species are severely disordered so the structure was subjected to the SQUEEZE procedure from the PLATON suite.[15] A void volume of 10129 Å (more than 20% of the unit cell volume) contained a minimum of 3614 electrons. Very low resolution data were not included in calculations of electron density in the void volumes, because of obscuration by the beam stop. Thus, the calculated number of electrons in the void volumes is substantially underestimated, and an interpretation of the electron count in terms of solvent species and the missing tetrafluoroborate anion has not been attempted. Prior to SQUEEZE, all non-hydrogen atoms were made anisotropic and all hydrogen atoms were inserted at their calculated positions, riding on the atoms to which they are attached with isotropic thermal parameters set to 1.2 times the equivalent isotropic displacement parameter for the attached non-hydrogen atom. After SQUEEZE, the refinement (SHELXL-97)[16] of 1399 parameters converged to R_1 = 0.0671 [for 10375 reflections having $F > 4\sigma(F)$], wR_2 = 0.2125 and goodness of fit 1.099 (for all 17147 F^2 data). Peak/hole 0.871 and –0.732 e $Å^{-3}$. After refinement, on recombining electron density in void volumes with final model, R1 ($I > 2\sigma(I)$) = 0.076.

Refinement was on F^2 against all reflections, retaining $F^2 < 0$. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2; conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating *R*-factors on "observed" data, and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger.

Because diffraction data did not extend beyond a resolution of 0.90 Å and were weak even at low resolution, extensive restraints were applied to the positional and atomic displacement parameters of the structure by means of FLAT, DFIX, ISOR, DELU and SIMU commands. The structure is notable for the high *U*(equiv) values of all atoms, including the silver(I) ions (Ag1-Ag4, *U*(equiv) in the range 0.0745(2)-0.0763(2); Ag5, *U*(equiv) = 0.0950(3). The large number of reflections that violated the systematic absences associated with *I* centering and the *a* glide plane is attributed to a less than stochastic disorder of solvent and anion species in the void volumes and of those parts of the grid complex that are disordered.

Crystal data for $[Ag_2(\mathbf{6})_2][BF_4]_2$ (Jrp50): $C_{24}H_{26}AgBF_4N_4$, M = 565.17, orange needles obtained by vapour diffusion of diethylether into a nitromethane solution, crystal dimensions 0.48 x 0.14 x 0.08 mm^3, monoclinic, P2(1)/c, a = 13.9951(2) Å, b = 8.19900(10) Å, c = 20.9379(3) Å, β = 98.3500(10), U = 2377.07(6) $Å^3$, μ = 0.899 mm^{-1}, Z = 4, D_c = 1.454 Mg/m^3 F(000) = 1144, T = 84(2) K. 12733 reflections were collected in the range $2.94° < 2\theta < 51.30°$. A semi-empirical absorption correction (SADABS) was applied (T_{max} = 0.910, T_{min} = 0.562). The 4466 independent reflections were used to solve the structure by direct methods (SHELXS-97).[14] The refinement (SHELXL-97)[16] of 313 parameters converged to R_1 = 0.0473 [for 3461 reflections having $F > 4\sigma(F)$], wR_2 = 0.1085 and goodness of fit 1.082 (for 4466 all F^2 data). Peak/hole 1.694 and –1.081 e $Å^{-3}$.

X-Ray data were collected on a Bruker SMART CCD diffractometer with graphite-monochromated Mo-Kα radiation. CCDC 263242 and 263243 contain the supplementary crystallographic data for this paper. These data can be obtained online free of charge from http://www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk

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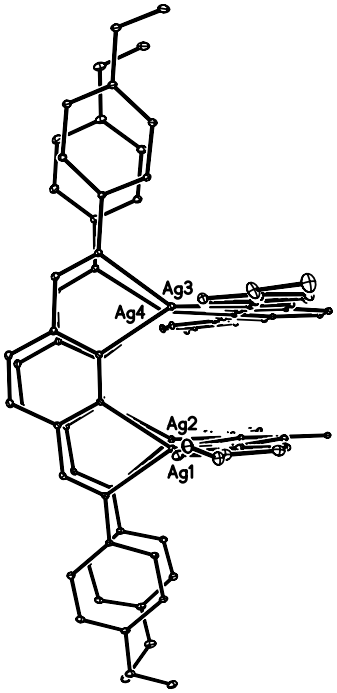

Figure S1. Alternative view of the $[C_2\text{-}Ag_4(\mathbf{5})_4]^{4+}$ grid.

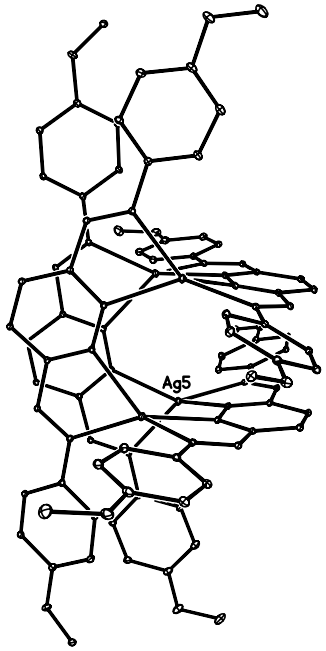

Figure S2. Alternative view of the $[S_4\text{-}Ag_4(\mathbf{5})_4]^{4+}$ grid.

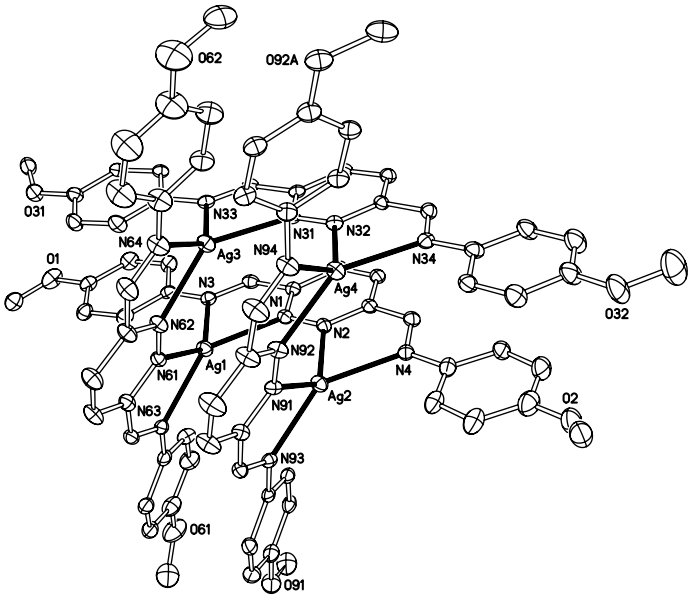

Figure S3. Another alternative view of the $[C_2\text{-}Ag_4(\mathbf{5})_4]^{4+}$ grid.

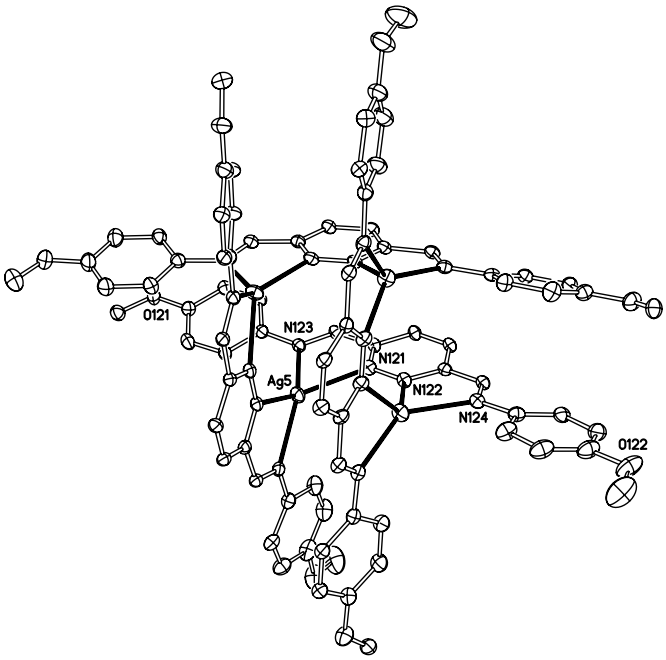

Figure S4. Another alternative view of the $[S_4\text{-}Ag_4(\mathbf{5})_4]^{4+}$ grid.