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A discrete dimer of coordination clusters connected through additional bridging ligands†

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The combination of directionality and unsaturated metal sites in bowl-shaped coordination clusters $[Ag_4L_3(SbF_6)]^{3+}$ {L = 2,4,6-*tris*(diphenylphosphino)triazine} results in the formation of discrete dimers on reaction with additional bridging ligands.

Metal ions and bridging organic ligands can be used as building blocks to self-assemble nanoscale coordination clusters.[1–6] Potentially, these aggregates could themselves be used as building blocks in the self-assembly of still larger, but discrete, coordination 'clusters of clusters'. However, this has been hindered by their general lack of: (i) well-defined external coordination sites,[2,3] and (ii) directionality (or more precisely polarity). Although bowl-shaped coordination clusters,[4] which are necessarily polar, have been deliberately synthesised, the topologies of coordination clusters are normally based on regular polygons or uniform polyhedra.[1] Upon further aggregation, the non-polar natures of these shapes would tend to give polymers rather than discrete assemblies.[3] In contrast, a polar bowl-shaped Pd coordination cluster has been assembled into a discrete dimer *via* guest-inclusion and hydrophobic forces,[4b] and a helical Cu cluster, which adopted a bowl-shaped conformation in the solid state, was found to pack as tetramers through π–π contacts.[5] We have recently reported the serendipitous formation of coordination clusters $[Ag_4L_3(\text{anion})]^{3+}$ {L = 2,4,6-*tris*(diphenylphosphino)triazine} based on partial tetrahedra (Fig. 1).[6] In these bowl-shaped complexes, the four Ag^+ ions form a distorted tetrahedron, but only three triphosphines are coordinated, leaving one face open with unsaturated AgP_2 metal sites. These could potentially be used to connect the bowls into larger discrete aggregates through bridging ligands.

Addition of 1.5 equivalents of 4,4′-dicyanobiphenyl to $[Ag_4L_3][SbF_6]_4$ in $CDCl_3$–CD_3NO_2 solution slightly altered the ^{31}P NMR signals for the AgP_2 centres (which changed from δ = 18.4 ppm and $^1J_{Ag-P}$ = 582 Hz to 17.3 ppm and 561 Hz) but had almost no effect on the signals of the AgP_3 centre at the base of the bowl (δ changed from 15.3 to 15.0 ppm, and $^1J_{Ag-P}$ remained 361 Hz), suggesting that the nitriles do coordinate at the open face. At low concentration (2.8 mmol l^{-1} in $[Ag_4L_3][SbF_6]_4$) the ^{31}P NMR spectrum corresponded to the uncomplexed bowl, suggesting that the coordination is weak and that there are equilibria between free and complexed bowls. When ether was allowed to diffuse into a solution, needle-shaped crystals were obtained, which were found to be the free, uncomplexed bowl (see Supplementary Information†). However, when benzene was used instead of ether, initially-formed needles were replaced over several weeks standing in the supernatant to give a mixture of block and hexagonal crystals. Although the hexagons were not amenable to single-crystal X-ray diffraction, they gave identical elemental analysis and IR and NMR spectra to the blocks. The blocks were found to be discrete centrosymmetric dimers in which two bowls are connected by two 4,4′-dicyanobiphenyl linkers (Figs. 1 and 2). The two bowl shaped units adopt an offset face-to-face arrangement to form a distorted dumb-bell structure. The eight Ag^+ ions describe two symmetry-equivalent distorted tetrahedra with Ag···Ag distances around the rim (average = 7.27(2) Å) which are longer than the rim-to-base distances (average = 6.15(2) Å). An SbF_6 anion is included in each bowl but Ag···F distances are all longer than 3 Å (shortest = 3.08 Å, to the uncomplexed AgP_2 centre) suggesting that there are no strong interactions between these anions and particular Ag^+ ions. The two crystallographically independent AgP_2N centres in each bowl unit have distorted trigonal-planar geometry with P···Ag···P angles of 140.8(2) and 143.7(2)°, and the sum of the three bond angles is 359.9(8)° in each case. The angular coordination of the C≡N–Ag groups (158.8(19) and 143.7(2)°, with N–Ag distances of 2.35(2) and 2.32(2) Å) is similar to that found in $[Ag(PPh_3)_2(NCCH_3)]^+$ (148.9(2)°, and 2.321(2) Å).[7] The P–Ag distances in the structure are normal.[7,8] The free AgP_2 centre has almost linear coordination with a P···Ag···P angle of 175.2(2)°. The AgP_3 centre has distorted trigonal-planar geometry (P···Ag···P angles = 113.4(2) – 123.2(2)°, the sum of P···Ag···P angles = 358.0(4)°). Between the biphenyl linking groups the two

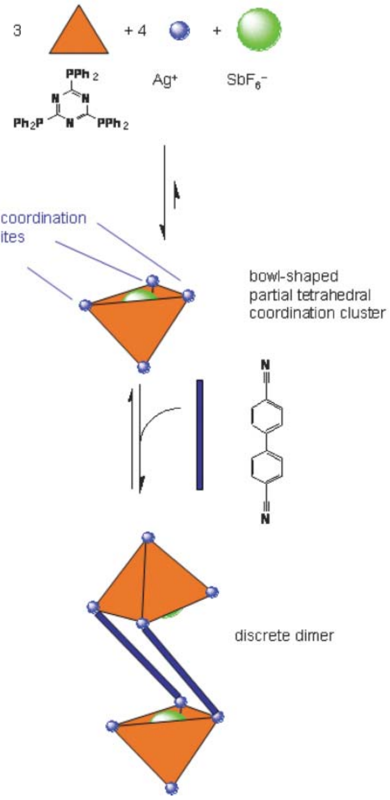

Fig. 1 Schematic showing the formation of bowl-shaped structures from silver ions and 2,4,6-tris(diphenylphosphino)triazine, and the connection of two bowls with bridging dinitriles.

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† Electronic supplementary information (ESI) available: crystal data for $C_{119}H_{88}N_9P_9Ag_4Sb_4F_{24}.3(NO_2CH_3).(CH_3CH_2)_2O.H_2O$. See http://www.rsc.org/suppdata/cc/b4/b409502b/

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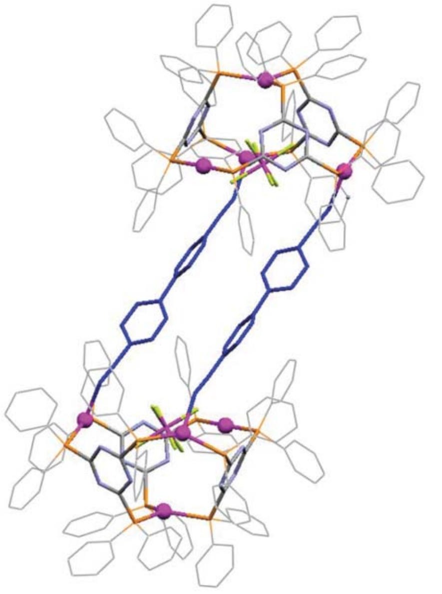

Fig. 2 X-ray crystal structure showing the cation $[\{Ag_4L_3(SbF_6)\}(4,4'\text{-dicyanobiphenyl})_2\{Ag_4L_3(SbF_6)\}]^{6+}$. Ag = pink, P = orange, N = light blue, F = yellow, C = grey, the bridging dinitriles are shown in blue and H's omitted for clarity.

closest C···C distances are both 3.72 Å, but the orientations of the bridging groups are not of the classical offset-face-to-face or edge-to-face π-stacking types.[9] The twist angle in the biphenyls of 35.4° (taken as the average of torsion angles C5S–C6S–C9S–C10S and C7S–C6S–C9S–C14S) is similar to those found in some other compounds containing the $NCC_6H_4C_6H_4CN$ unit.[10] Overall the slanted dumb-bell structure is *ca.* 3.69(2) nm end-to-end (taken from the H82···H82A distance of 3.45(2) nm, plus H van der Waals radii of 0.120 nm).[11]

In summary, self-assembled bowl-shaped Ag_4L_3 aggregates are directional with unsaturated metal centres and so can be linked together to form *discrete* aggregates. Studies toward higher oligomers (*e.g.* tetramer, hexamer *etc.*) are in progress.‡

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Notes and references

‡ Synthesis: A solution of 2,4,6-*tris*(diphenylphosphino)triazine[6] (165.0 mg, 0.26 mmol) in $CHCl_3$ (9 ml) was added to a solution of $AgSbF_6$ (119.4 mg, 0.35 mmol) in nitromethane (3 ml), to which was then added solid 4,4′-dicyanobiphenyl (26.6 mg, 0.13 mmol). The resulting solution was layered with benzene to give initially needle shaped crystals, which redissolved after several weeks to give a mixture of block- and hexagonal-shaped crystals. Yield 250 mg, 83%. Microanalysis (after drying *in vacuo*): found (calc.) for $Ag_8L_6(SbF_6)_8(4,4'\text{dicyanobiphenyl})_2$ C 44.93 (45.22), H 2.82 (2.84), 4.12 (4.43). IR (Nujol, cm^{-1}): 2252sh, 2241 (v CN), 656 (SbF_6). X-ray crystallographic data for the title compound were collected using a Bruker SMART diffractometer with graphite monochromated Mo–K_α radiation. The crystal stability was monitored and there was no significant decay (±1%). Data were collected at low temperature *ca.* 153 K. Omega\phi scans were employed for data collection and absorption, Lorentz and polarisation corrections were applied. The structure was solved by direct methods and ordered non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Hydrogen-atom positions were added and idealised positions and a riding model with fixed thermal parameters ($U_{ij} = 1.2U_{eq}$ for the atom to which they are bonded (1.5 for CH_3)), was used for subsequent refinements. Examination of the atomic displacement parameters for the phenyl ring shows that some of them may be disordered. However, attempts to model this disordered were unsuccessful and subsequently these rings were restrained to adopt an appropriate geometry using the DFIX, FLAT and SIMU instructions in SHELXTL.[9] The function minimised for wR2 was $S[w(|F_o|^2 - |F_c|^2)]$ with reflection weights $w^{-1} = [\sigma^2 |F_o|^2 + (g_1P)^2 + g_2P]$ where $P = [\max |F_o|^2 + 2|F_c|^2]/3$ for all F^2 and the function minimised for R1 was $\Sigma[w(|F_o| - |F_c|)]$. The SAINT[13] and SHELXTL[12] packages were used for data collection, reduction, structure solution and refinement. Additional material available from the Cambridge Structural Database includes atomic co-ordinates, thermal parameters, remaining bond lengths and angles, and structure factors CCDC 242989 and 247596. See http://www.rsc.org/suppdata/cc/b4/b409502b/ for crystallographic data in .cif or other electronic format. Crystal data for $C_{262}H_{196}N_{22}P_{18}Ag_8Sb_8F_{48}.3(NO_2CH_3)\cdot(CHCl_3)\cdot 2H_2O$: - $M = 7294.36$, monoclinic, space group $P2_1/c$, $a = 24.491(11)$, $b = 17.774(8)$ Å, $c = 35.165(16)$ Å, $\beta = 94.920(11)°$, $U = 15251(12)$ Å^3, $Z = 2$, $Dc = 1.588$ Mg m^{-3}, $F(000) = 7160$, $\mu = 1.401$ mm^{-1}, crystal dimensions = 0.34 × 0.20 × 0.17 mm. A total of 144575 reflections were measured for $2 < 2\theta < 50$ and 26831 unique reflections were used in the refinement, the final parameters were $wR2 = 0.3041$ and $R1 = 0.1019$ $[I > 2\sigma(I)]$.

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