

Polar Self-Assembly: Steric Effects Leading to Polar Mixed-Ligand Coordination Cages

Jianyong Zhang, Philip W. Miller, Mark Nieuwenhuyzen, and Stuart L. James*^[a]

Abstract: We present a highly unusual example of self-assembly, specifically a polar, mixed-ligand cage which forms in preference to symmetrical homo-ligand products, and which suggests that steric effects can be exploited to obtain novel non-uniform polyhedral cages. In particular, reaction between the bulky tripodal triphosphine 2,4,6-tris(diphenylphosphino)triazine, L1, the non-bulky tripodal trinitrile 2,4,6-tris(cyanomethyl)trimethylbenzene, L2 and silver hexafluoroantimonate, AgSbF₆, in a 3:1:4 ratio gives the mixed-ligand aggregate [Ag₄(L1)₃(L2)(SbF₆)]³⁺, **1**-SbF₆, instantly as the only product in quantitative yield. The X-ray crystal structure of complex **1**-SbF₆ is consistent with the suspected solution-state structure. The cage derives

from trigonal-pyramidal geometry, the basal vertices of which are defined by three bulky triphosphines, L1, and the apical vertex by the non-bulky trinitrile, L2. There is apical elongation amounting to 19% in comparison to the ideal uniform tetrahedron. The cage also encapsulates an SbF₆ anion. ¹⁹F NMR spectra in solution for the analogous PF₆ complex [Ag₄(L1)₃(L2)(PF₆)]³⁺, **1**-PF₆, confirm that one anion is also encapsulated in solution. The synthesis of the analogous CF₃SO₃⁻ complex, [Ag₄(L1)₃(L2)(OTf)]³⁺, **1**-OTf, in solution is also described, although **1**-PF₆ and **1**-OTf could not be

isolated due to slow decomposition in solution. The selective formation of these mixed-ligand cages is discussed in terms of ligand–ligand and ligand-included anion steric repulsions, which we propose prevent the formation of the competing hypothetical homo-ligand tetrahedral structure [Ag₄(L1)₄(SbF₆)]³⁺, and thus favour the mixed ligand cage. “Cage cone angles” for L1 and L2 are estimated at 115° and 101°, respectively. Variable-temperature ³¹P NMR spectroscopy shows that complex **1**-SbF₆ and the related previously reported partial tetrahedral complex [Ag₄(L1)₃(anion)]³⁺ undergo dynamic twisting processes in solution between enantiomeric C₃-symmetry conformations.

Keywords: anions • cages • phosphane • self-assembly

Introduction

Although coordination-based self-assembly has been demonstrated as an effective way to prepare large, multimetallic cages and rings, these structures are normally restricted to being highly symmetrical and non-polar.^[1] For example, large coordination cages reported to date are normally based on uniform polyhedra, that is, those in which all the vertices are identical, such as the Platonic and Archimedean classes.^[1] Ways to selectively obtain polar cages would signif-

icantly widen the scope of this chemistry. For example, polar shapes would have different guest inclusion characteristics, and, as we have previously shown, their directionality can be exploited to assemble still larger, discrete coordination clusters of clusters.^[2] One strategy to obtain polar shapes is to take a uniform polyhedral structure and formally replace, in a controlled and selective way, one or more of the bridging ligands with a different type of bridging ligand. However, when mixtures of different bridging ligands are allowed to react with labile metal ions in one pot, normally homo-ligand aggregates are obtained instead (i.e. the ligands “self-select”).^[1,3] To our knowledge, only a small number of exceptions to this general behaviour have been described.^[4] In one case a non-polar mixed-ligand aggregate was obtained selectively due to the template effect of an appropriately shaped guest molecule.^[4a] Most relevant to our work described herein, other mixed-ligand, but non-polar, structures have been obtained selectively by combining bulky and non-bulky ligands. The principle of this approach, as illustrated

[a] Dr. J. Zhang, Dr. P. W. Miller, Dr. M. Nieuwenhuyzen, Prof. S. L. James
Centre for the Theory and Application of Catalysis
School of Chemistry, Queen's University Belfast
David Keir Building, Stranmillis Road, Belfast BT9 5 AG
Northern Ireland (UK)
E-mail: s.james@qub.ac.uk

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by the study of mixed-component trimers by Severin et al.,^[4b] is that coordinatively saturated structures based only on the bulky component are sterically disfavoured, and this forces the system to form aggregates based on both bulky and non-bulky building blocks (i.e. it prevents self-selection). Examples of cages prepared by using this approach, which contain a mixture of ligands, but which are still non-polar, are the cylinders reported by Lehn et al.,^[4c] and a polar tetrapalladium mixed-ligand capsule reported recently by Kobayashi et al.^[4d] The most systematic use of this approach is by Schmittel et al.^[4e] who have employed phenanthrolines with bulky substituents to favour the formation of heteroleptic complexes (the HETPHEN approach) and thus have rationally prepared non-regular, but still non-polar, polygons such as rectangles and ladders.^[4e]

In recent years we have exploited bridging di- and triphosphines as novel building blocks for the self-assembly of discrete coordination cages as well as infinite coordination polymers (metal-organic frameworks).^[2,5-7] Triarylphosphines are unusually bulky ligands for coordination-based self-assembly and have given rise to some interesting results. For example, most recently we have found that the triazine-cored tripodal ligand tris(diphenylphosphino)triazine, L1, reacts with silver ions to give, selectively, the unsaturated *partial* tetrahedral bowl-shaped structure $[\text{Ag}_4(\text{L1})_3(\text{X})]^{3+}$ ($\text{X} = \text{OTf}, \text{SbF}_6$), which has a metal-to-ligand ratio of 4:3.^[2,6] This compound is unusual in being an unsaturated, open, polar structure. Interestingly, the expected “conventional” complete tetrahedral structure $[\text{Ag}_4(\text{L1})_4(\text{X})]^{3+}$, with a metal-to-ligand ratio of 4:4, was not observed even when additional L1 was added. This unusual behaviour can be ascribed to significant ligand–ligand and/or ligand–anion steric repulsion, which is exacerbated by the presence of bulky phenyl groups on the ligands.

We report here the addition of a non-bulky tripod to this “incomplete” structure as a way to form, with high selectivity, a closed, mixed-ligand cage. This closed cage is noteworthy because in contrast to most coordination cages it is not based on a uniform polyhedron, and furthermore it is polar. It also provides further insight into the role of sterics in stabilizing unusual self-assembled cages.

Results and Discussion

When tris(diphenylphosphino)triazine L1,^[2,6] and the non-bulky tripodal trinitrile 2,4,6-tris(cyanomethyl)trimethylbenzene, L2, are mixed with AgPF_6 in the appropriate 3:1:4 ratio in $\text{CDCl}_3/\text{CD}_3\text{NO}_2$, a single species is formed quantitatively, as indicated by ^{31}P NMR spectroscopy, which corresponds to the trigonal-pyramidal, or “capped bowl” structure $[\text{Ag}_4(\text{L1})_3(\text{L2})\text{PF}_6]^{3+}$, **1-PF₆**. For reference, the X-ray crystal structure of the analogous SbF_6^- complex $[\text{Ag}_4(\text{L1})_3(\text{L2})\text{SbF}_6]^{3+}$ **1-SbF₆**, which is described more fully below, can be seen in Figure 1. The ^{31}P NMR spectrum of **1-PF₆** shows the presence of an AgP_3 centre at $\delta = 15.5$ ppm, with $^1J_{109\text{Ag},31\text{P}} = 363$ Hz, as well as AgP_2N centres at $\delta =$

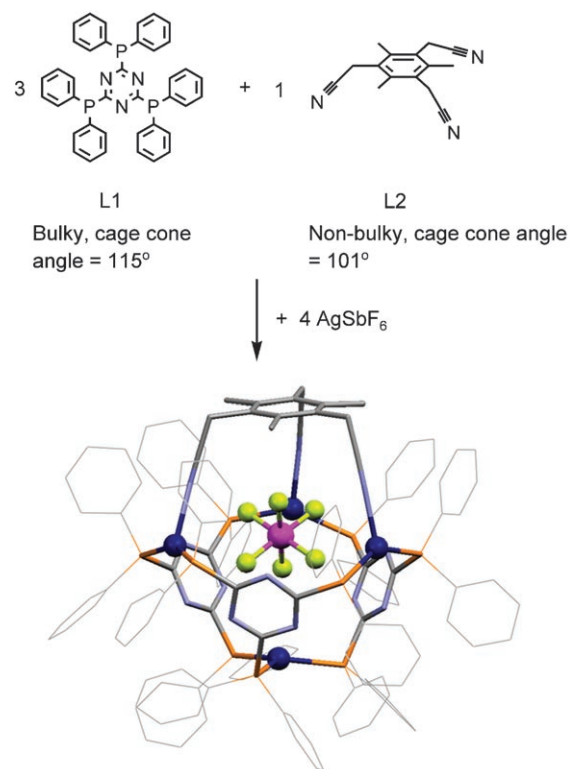


Figure 1. Synthesis and X-ray crystal structure of the mixed-ligand cage complex $[\text{Ag}_4(\text{L1})_3(\text{L2})(\text{SbF}_6)]^{3+}$ **1-SbF₆** (Ag: dark blue; P: orange; N: light blue; Sb: pink, F: green). Hydrogen atoms are omitted for clarity.

13.7 ppm, with $^1J_{109\text{Ag},31\text{P}} = 532$ Hz. The ^{19}F spectrum shows one encapsulated PF_6^- anion ($\delta = -74.5$ ppm) and three free PF_6^- anions ($\delta = -73.8$ ppm). The ^1H NMR signals of L2 are shifted in the complex ($\delta = 3.99$ ppm, CH_2 ; $\delta = 2.38$ ppm, CH_3) compared to the free ligand ($\delta = 3.74$ and 2.46 ppm). Compound **1-PF₆** decomposed slowly in solution and X-ray-quality crystals could not be obtained. However, NMR data suggested that similar capped structures, **1-SbF₆** and **1-OTf**, were formed when AgSbF_6 or AgOTf were used in place of AgPF_6 , although the ^{31}P signals for the AgP_2N centres were broader for both of these complexes. We relate this broadness to a dynamic twisting of the structure between enantiomeric C_3 -symmetry conformations as described below. Crystals of **1-SbF₆** were obtained by layering a $\text{CDCl}_3/\text{CD}_3\text{NO}_2$ solution with benzene, and were solved by X-ray crystallography (Figure 1), which confirmed the suspected mixed-ligand cage structure with an encapsulated SbF_6^- anion. The $\text{Ag}_4(\text{L1})_3$ fragment of **1-SbF₆** is not greatly distorted compared to the previously characterised “free bowl” complex $[\text{Ag}_3(\text{L1})_4(\text{OEt}_2)(\text{SbF}_6)]^{3+}$.^[6] However, incorporation of the trinitrile as a lid does result in the SbF_6^- anion shifting further away from the base of the cavity ($\text{AgP}_3 \cdots \text{Sb} = 4.58$ Å for **1-SbF₆** and 4.42 Å for $[\text{Ag}_3(\text{L1})_4(\text{OEt}_2)(\text{SbF}_6)]^{3+}$).^[5] Within **1-SbF₆** there are shorter $\text{F} \cdots \text{Ag}$ distances from the encapsulated anion to the AgP_2N centres (2.71, 2.83, 3.15 Å) than to the AgP_3 centre (shortest = 3.29 Å), suggesting greater interaction with the former. The SbF_6^- anion lies in the same plane as the three AgP_2N centres with $\text{Ag-Sb-Ag}_{\text{rim}}$ angles

of 118.5, 120.0, 121.4° (sum = 359.9°). In its capping coordination mode, the trinitrile is slightly distorted at the CH₂ groups (C...CH₂...C angles are 107.6, 110.7, 111.0°) to allow it to coordinate simultaneously to the three Ag centres, and the C=N-Ag angles are distorted from linearity at 163.2, 168.5 and 175.6°. The angles at the AgP₂N coordination centres reveal approximately planar coordination (average sum = 359.1°) but with significant distortion from regular trigonal-planar geometry.

The space-filling view of **1-SbF₆** in Figure 2 shows how the steric bulk of the three triphosphine ligands (L1 = red, green, and light brown) leaves only a small region for the

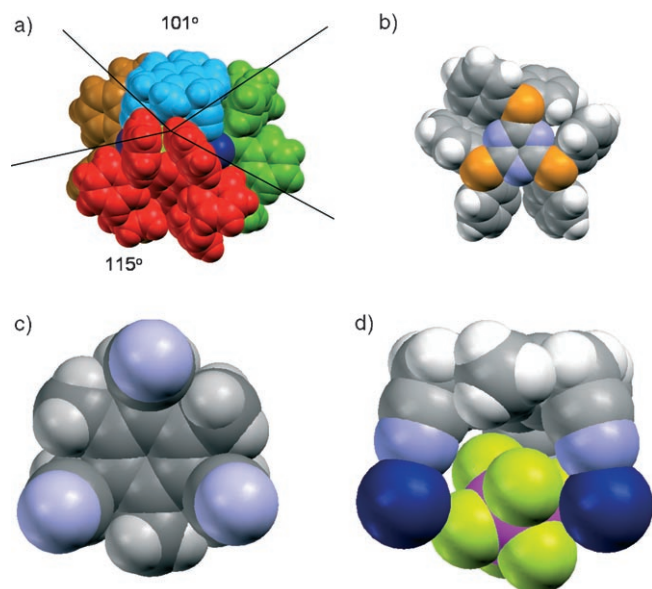


Figure 2. The space-filling views showing: a) cage **1-SbF₆** with “cage cone angles” (trinitrile = light blue, triphosphines = red, green, brown); b) and c) comparison of the sizes of L1 and L2, and d) part of the structure showing how the extended reach of L2 allows room for the anion.

fourth ligand (L2 = light blue) to complete the polyhedral structure. We have previously found that L1 itself is unable to form the hypothetical complete closed tetrahedral structure [Ag₄(L1)₄(SbF₆)]³⁺,^[6] even on addition of excess L1. The limited remaining space in the partial tetrahedral structure is clearly sufficient however for the sterically non-demanding trinitrile ligand L2. “Cage cone angles” (i.e. the cluster cone angle^[8] concept applied in this case to a coordination cage) give a rough comparison of the different ligand sizes, even though the shape of L1 is rather irregular. They were estimated for the two ligands by taking the included Sb centre as the cage centroid, and representative angles to the outermost diametrically opposed atoms in the ligands. For L2 a CH₃...Sb...CH₂ distance was taken (where the CH₃ and CH₂ groups are mutually *para*), specifically H13 K...Sb1...C133 = 70.4°, and for L1 phenyl H atoms, specifically H20A...Sb1...H32A = 94.8°. Taking into account the van der Waals radii of carbon and hydrogen (1.70 and 1.20 Å, respectively^[9]) then gives more realistic cage cone

angles of 101° for L2 and 115° for L1.^[10] It is interesting that for L1 the cage cone angle exceeds the theoretical maximum for the formation of a tetrahedral coordination cage (109°).

A further factor which may be important in allowing the complete closed cages to form is the greater reach of L2 compared to that of L1. In particular, each arm of L2 has two additional carbon spacer atoms between the coordinating atom and the central ring, than in L1 (in which the P centres connect directly to the triazine core). These additional spacers may be important in allowing sufficient room for anion encapsulation in, and therefore stabilisation of, the closed structures **1**. In fact the closest distance between an F atom of the included anion, and a C atom of the central ring of L2 in **1-SbF₆** is 3.31 Å (F14...C140). This is only slightly larger than the combined F and C van der Waals radii^[9] (1.47(F) + 1.70(C) = 3.17 Å). Figure 2 (bottom) illustrates that there is still a reasonably tight fit for the anion. Accordingly we investigated whether the use of smaller anions might allow the previously unobserved homo-ligand tetrahedral cage [Ag₄(L1)₄(anion)]³⁺ to form. Halides Cl⁻, Br⁻ or I⁻, as their tetrabutyl ammonium salts, were added to equimolar solutions of AgSbF₆ and L1. In addition, equimolar solutions of AgNO₂ and L1 were studied. In all cases room temperature ³¹P NMR spectra showed broad singlets without evidence of coupling to ¹⁰⁷Ag and ¹⁰⁹Ag. In each case, on cooling the samples, complicated spectra consisting of large numbers of peaks were observed, from which no structural assignments could be made, and suggesting that mixtures of several complexes were present. Although it cannot be ruled out that these mixtures contained small amounts of the symmetrical tetrahedral cages [Ag₄(L1)₄(anion)]³⁺ (anion = Cl, Br, I, NO₂) they were clearly not formed with any appreciable degree of selectivity. This observation supports the argument that ligand-ligand steric repulsion, rather than ligand-included anion steric repulsion, is the reason for the instability of the homo-ligand tetrahedral cage. However, it should also be noted that with these small anions, we did not observe partial tetrahedral structures [Ag₄(L1)₃(anion)]³⁺, which are the main species present under the same conditions when larger anions (SbF₆, OTf) are used.^[6] This therefore points instead to the complication that there is actually an active templating effect of these smaller, more nucleophilic anions. Through their stronger coordination to the silver centres, they apparently stabilise instead mixtures of other complexes. Anion templating effects are to be expected since we have previously observed them in adamantoid triphosphine-silver cages.^[7]

Whereas most polyhedral coordination cages have identical vertices (i.e. they are derived from uniform polyhedra), the mixed-ligand cages **1-PF₆**, **1-SbF₆** and **1-OTf** described here have non-identical vertices and so are formally derived from a non-uniform polyhedron, the trigonal pyramid. The effect of this lower symmetry on the interior dimensions of **1-SbF₆** can be seen from the shape defined by the centroids of the four capping ligands (Figure 3). This pyramid has an average basal edge length of 6.53 Å (L1 to L1 distances)

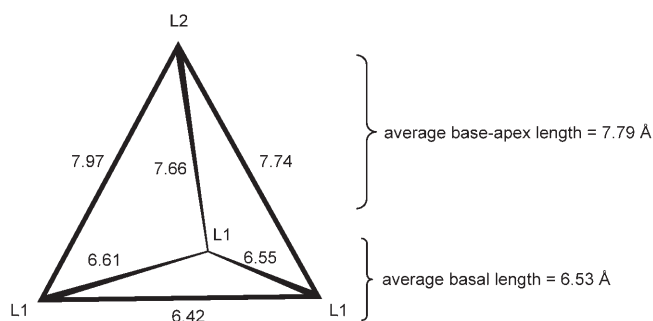


Figure 3. The trigonal pyramid described by the centroids of the four ligands of complex **1**, with distances in angstroms.

and average base-to-apex length of 7.79 Å (L1 to L2 distances) which amounts to a stretching of 19% compared to the “ideal” tetrahedron.

We also studied the effect of varying the stoichiometry of the reagents on the assembly of the cage. In principle, a range of non-uniform structures can be accessed by further formal replacement of the triphosphine for trinitriles. In fact, in this case, use of a 2:2:4 stoichiometry (L1:L2:Ag) gave cage **1** as the only identifiable peaks in the ^{31}P NMR spectrum. Increasing the amount of L1 to a stoichiometry of 4:1:4 or L2 to a stoichiometry of 3:2:4 also gave only cage **1** according to ^{31}P NMR spectroscopy. In the latter case, the free and coordinated L2 could not be distinguished by ^1H NMR spectroscopy, suggesting that there was fast exchange on the NMR timescale. Lastly, the formation of **1** was also found to be independent of the overall concentration, that is, there was no evidence of higher oligomers **1**₂, or **1**₄ at high concentration.

Dynamic behaviour: As stated above, in contrast to the sharp ^{31}P NMR spectrum of **1**-PF₆, **1**-SbF₆ showed some broadening in its ^{31}P NMR spectrum at room temperature (Figure 4). Whilst the signals due to the AgP₃ centre are sharp, and couplings to both ^{107}Ag and ^{109}Ag isotopes are resolved, the signals for the AgP₂N centres (at $\delta \approx 15.5$ and

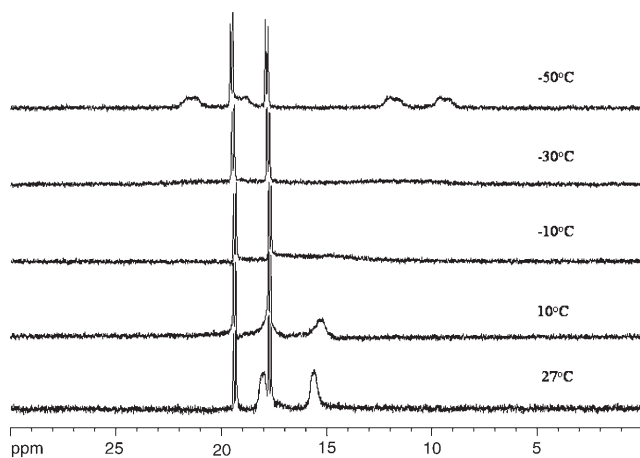


Figure 4. Variable-temperature ^{31}P NMR spectra of cage complex **1**-SbF₆.

17.0 ppm) are broadened sufficiently so that signals due to the individual ^{107}Ag and ^{109}Ag isotopomers are not resolved. To probe any dynamic behaviour of this structure, low-temperature spectra were obtained. As the temperature is lowered, the broadness of these signals increases until from -10 to -30°C only very broad features close to the baseline are visible. At -50°C new broad signals emerge from the baseline at $\delta \approx 21.5$, 19.0, 11.8 and 9.5 ppm which appear from their positions to show evidence of P-Ag coupling, although again signals due to the ^{107}Ag and ^{109}Ag isotopomers are not resolved. Overall, the spectra can be explained by a dynamic twisting of the cage structure, in which enantiomeric C_3 -symmetry conformations interconvert quickly at higher temperatures, but slowly at low temperature. In this way, the two P atoms at each AgP₂N centre become inequivalent (P_B and P_C in Figure 5) at low temperature.

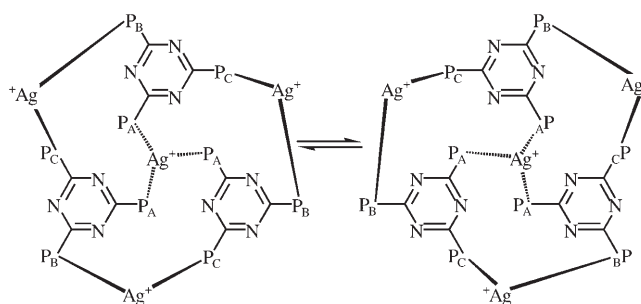


Figure 5. Interconversion by twisting between C_3 -symmetry conformations which renders the P centres at each AgP₂N centre inequivalent in the slow exchange regime. The capping trinitrile ligand has been omitted for clarity.

We also investigated the previously reported partial tetrahedral aggregate [Ag₄(L1)₅(OTf)](OTf)₃ with regard to any dynamic behaviour and analogous spectra were observed (Figure 6). The room temperature spectrum in this case is complicated by the coincidence of signals due to the AgP₃ and AgP₂ centres (at $\delta \approx 16$ ppm). However, as the temperature is lowered, only the signals due to the AgP₂ centres become broad. At -70°C the process is sufficiently slow that signals due to the inequivalent P atoms are fully resolved, and this part of the spectrum then appears as the superposition of two ABX spin systems (one for each Ag isotope). $^1J_{\text{Ag,P}}$ for each P atom in the AgP₂ centres is 501 Hz, and $^2J_{\text{PP}}$ through the Ag centre is 81 Hz. We are unaware of previous reports of $^2J_{\text{PP}}$ coupling through a silver centre. Spectra run at one degree intervals between -19 and -23°C gave a coalescence temperature of -22°C , which corresponds to a Gibbs free energy of activation for the twisting process of 43.8 kJ mol⁻¹ from the Eyring equation.

A further point is whether the polarity of the structure is manifested in the ^{19}F spectrum of the included PF₆ anion. However, at low temperatures we saw no evidence for any inequivalence of the F nuclei, indicating that tumbling of anion was not frozen out or that the asymmetry does not alter the chemical shifts of the individual F atoms.

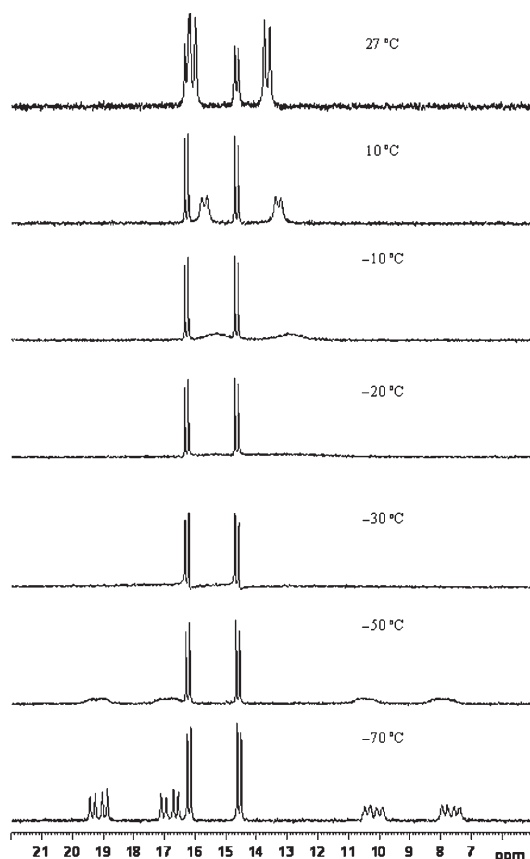


Figure 6. Variable-temperature ^{31}P NMR spectra for the partial tetrahedral complex $[\text{Ag}_4(\text{L1})_3(\text{OTf})(\text{OTf})_3]$.

Conclusion

A highly unusual, polar coordination cage has been found to assemble selectively from a mixture of bulky and non-bulky ligands and silver ions. Steric destabilisation of the competing hypothetical homo-ligand aggregate $[\text{Ag}_4(\text{L1})_4(\text{anion})]^{3+}$ appears to be the key to the selective formation of this unusual structure. Clearly, the exploitation of steric effects provides a way to extend the self-assembly of polyhedral cages toward less regular, even polar, structures, which are not obtained using current “non-bulky” methodologies.

Experimental Section

General: Reagents were purchased from Aldrich and used as supplied unless otherwise stated. L1 was prepared as previously described.^[6] ^{31}P NMR spectra were recorded at 121.5 MHz and 27 °C unless otherwise stated, and are referenced to external H_3PO_4 (aq) 85%.

Synthesis of complex 1-SbF₆: Solid 2,4,6-tris(diphenylphosphino)triazine (L1) (130.6 mg, 0.21 mmol) and 1,3,5-tris(cyanomethyl)-2,4,6-trimethylbenzene (L2)^[11] (16.3 mg, 0.069 mmol) were added to a solution of AgSbF_6 (94.5 mg, 0.275 mmol) in CHCl_3 (3 mL) and CH_3NO_2 (1 mL). The resulting solution was layered with benzene to give block- and needle-shaped crystals. Yield 215 mg, 89%. Elemental analysis (after drying in vacuo) calcd (%) for $[\text{Ag}_4(\text{L1})_3(\text{SbF}_6)_4(\text{L2})]$: C 45.14, H 3.01, N 4.79; found: C 45.65, H 3.33, N 4.58; ^{31}P NMR (121.5 MHz, $\text{CDCl}_3/\text{CD}_3\text{NO}_2$, 3:1, 25 °C): $\delta = 14.7$ ($^1J_{\text{Ag},^{31}\text{P}} = 361$ Hz), 12.9 ppm; ^1H NMR

(300 MHz): $\delta = 7.61\text{--}7.04$ (m, 96H; Ph), 6.43 (t, 12H; Ph), 3.97 (s, 6H; CH_2), 2.30 ppm (s, 9H; CH_3); IR (Nujol): $\tilde{\nu} = 2272$ ($\nu(\text{CN})$), 655 ($\nu(\text{SbF}_6)$) cm^{-1} .

Synthesis of complex 1-PF₆: Solid L1 (32.3 mg, 0.051 mmol) and L2 (4.0 mg, 0.017 mmol) were added to a solution of AgPF_6 (17.2 mg, 0.068 mmol) in CDCl_3 (2 mL) and CD_3NO_2 (0.5 mL). The solution obtained was used for NMR spectroscopy. ^{31}P NMR (121.5 MHz, $\text{CDCl}_3/\text{CD}_3\text{NO}_2$, 3:1): $\delta = 15.5$ ($^1J_{\text{Ag},^{31}\text{P}} = 363$ Hz), 13.7 ppm ($^1J_{\text{Ag},^{31}\text{P}} = 532$ Hz); ^{19}F NMR (282 MHz, $\text{CDCl}_3/\text{CD}_3\text{NO}_2$, 3:1): $\delta = -73.8$ ($^1J_{^{19}\text{F},^{31}\text{P}} = 709$ Hz, free PF_6^-), -74.5 ppm ($^1J_{^{19}\text{F},^{31}\text{P}} = 726$ Hz, encapsulated PF_6^-); ^1H NMR (300 MHz, $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{NO}_2$, 3:1): $\delta = 7.64\text{--}7.17$ (m, 90H; Ph), 7.11 (t, 6H; Ph), 6.50 (t, 12H; Ph), 3.99 (s, 6H; CH_2), 2.38 ppm (s, 9H; CH_3). 193 K: ^{19}F NMR (282 MHz, $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{NO}_2$, 3:1): $\delta = -73.3$ ($^1J_{^{19}\text{F},^{31}\text{P}} = 710$ Hz, free PF_6^-), -76.3 ppm ($^1J_{^{19}\text{F},^{31}\text{P}} = 726$ Hz, encapsulated PF_6^-); ^1H NMR (300 MHz, $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{NO}_2$, 3:1): $\delta = 7.63\text{--}6.86$ (m, 105H; Ph), 6.58 (s, 3H; Ph), 4.06 (s, 3H; CH_2), 3.77 (s, 3H; CH_2), 2.32 (s, 9H; CH_3).

Synthesis of complex 1-OTf: The procedure was analogous to that of **1-PF₆**. ^{31}P NMR (121.5 MHz, $\text{CDCl}_3/\text{CD}_3\text{NO}_2$, 3:1): $\delta = 15.8$ ($^1J_{\text{Ag},^{31}\text{P}} = 360$ Hz), 12.7 ppm; ^1H NMR (300 MHz): $\delta = 7.69\text{--}7.21$ (m, 90H; Ph), 7.09 (t, 6H; Ph), 6.47 (t, 12H; Ph), 4.07 (s, 6H; CH_2), 2.32 ppm (s, 9H; CH_3); ^{19}F NMR (282 MHz, $\text{CDCl}_3/\text{CD}_3\text{NO}_2$, 3:1): $\delta = -75.9$ (free OTf^-), -74.9 ppm (coordinated OTf^-).

Synthesis of L2: This was by a modified procedure of Podlaha et al.^[11] NaCN (0.892 g, 18.2 mmol) was dissolved in DMSO (30 mL) at 40 °C. A solution of 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene (2.394 g, 6.0 mmol) in DMSO (30 mL) was then added slowly over 2 h. The reaction mixture was stirred for 20 h at 40 °C, then poured into ice-water (40 mL) and extracted with Et_2O and CH_2Cl_2 . The combined organic layers were washed with brine, dried and concentrated to give a colourless solid (0.44 g, 31%). Elemental analysis calcd (%) for $\text{C}_{15}\text{H}_{15}\text{N}_3$: C 75.92, H 6.37, N 17.71; found: C 75.44, H 6.93, N 17.49; ^1H NMR (300 MHz, CDCl_3): $\delta = 3.74$ (s, 6H; CH_2), 2.46 ppm (s, 9H; CH_3).

Halide and nitrite reactions: A solution of L1 (63.3 mg, 0.10 mmol) in CDCl_3 (2 mL) was added to a suspension of AgNO_2 (15.4 mg, 0.10 mmol) in CD_3NO_2 (0.5 mL). The mixture was stirred for 30 min. A trace amount of insoluble material was removed by filtration and the resulting solution was examined by NMR spectroscopy (^{31}P NMR (121.5 MHz, $\text{CDCl}_3/\text{CD}_3\text{NO}_2$, 3:1): $\delta = 15.5$ ppm (br.) plus other minor peaks). Reactions with halides performed similarly with equimolar quantities of AgSbF_6 , L1, and NBu_4X (X = halide) as the halide source.

X-ray crystallographic data:^[12,13] ($\text{C}_{163}\text{H}_{149.50}\text{Ag}_4\text{F}_{24}\text{N}_{17}\text{O}_{11}\text{P}_9\text{Sb}_4$): $M_r = 4175.71$, monoclinic, space group $P2_1/c$, $a = 18.1599(16)$, $b = 30.704(3)$, $c = 31.043(3)$ Å, $\beta = 98.872(3)^\circ$, $U = 17103(3)$ Å³, $Z = 4$, $\mu = 1.242$ mm⁻¹, $R_{\text{int}} = 0.1116$. A total of 197543 reflections were measured for the angle range $2 < 2\theta < 57^\circ$, and 40379 independent reflections were used in the refinement. The final parameters were $wR2 = 0.3186$ and $R1 = 0.1288$ [$I > 2\sigma(I)$]. Some of the solvent molecules and SbF_6^- anions showed evidence of disorder. The residual peaks in the final difference map are associated with these disordered regions. The disordered anion was modeled as occupying two sites with occupancy of 50%. Attempts at modeling the disorder of the solvent molecules were unsuccessful and thus the solvents were restrained and given full occupancy except for the ethanol molecule which is disordered about an inversion centre and has an occupancy factor of 50%.

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