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Stepwise assembly of an adamantoid Ru₄Ag₆ cage by control of metal coordination geometry at specific sites†

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The geometrically pure 'complex ligand' *fac*-[Ru(L^{ph})₃]²⁺, in which three pendant bidentate binding sites are located on one face of the complex, reacts with Ag(I) ions to form the adamantoid decanuclear cage [(Ru(L^{ph})₃)₄Ag₆](PF₆)₁₄ which contains a 6-coordinate Ru(II) ion at each vertex of a large tetrahedron and a 4-coordinate Ag(I) ion along each edge.

The self-assembly and host-guest chemistry of metal-ligand coordination cages continue to fascinate. Such high-symmetry cages represent appealing synthetic targets for supramolecular chemists to test their skills at controlling self-assembly so as to generate elaborate, multi-component assemblies from simple starting materials.¹ In addition the ability of cages to bind guest molecules in their central cavity leads to potential applications² ranging from catalysis³ to drug delivery.⁴

The vast majority of cages are formed from just two types of component: one type of metal ion and one type of ligand. A few examples of mixed-ligand cages are known in which the self-assembly process specifically occurs with selection of two different types of ligand, resulting in a heteroleptic complex being favoured over the homoleptic alternatives.⁵ Likewise a few examples of mixed-metal cages exist in which two different types of metal ion occupy different vertex positions in a cage structure.^{6–8} This can occur when the two types of metal ion have different geometric preferences and the self-assembly requires both: for example, octahedral tris-chelate metal ions at the vertices of a cube and square planar ions with four monodentate ligands at the face centres.⁷ Alternatively, we showed recently how different types of metal ion can be positioned at specific sites in a polyhedral array if kinetically inert metal complex subcomponents

are prepared first and then combined with a second labile metal ion to complete the assembly in a stepwise manner.⁸

Our extensive family of polyhedral cage complexes generally contain an octahedral tris-chelate metal ion at each vertex, and a bis-bidentate bridging ligand (containing two pyrazolyl-pyridine chelating termini) along each edge.^{1c} In these complexes the geometric isomerism (*fac* vs. *mer*) of the metal centres turns out to play a crucial role in the nature of the assembly that forms. In some complexes, such as a family of M₄L₆ tetrahedra, all four metal centres have a *fac* tris-chelate geometry;⁹ in contrast, in a series of M₁₂L₁₈ truncated tetrahedra, all metal centres have a *mer* tris-chelate geometry.¹⁰ In several other types of cage assembly however there is a 3 : 1 mixture of *mer*:*fac* tris-chelate vertices.¹¹ Therefore, the ability to control the self-assembly of such cages – particularly mixed-metal versions – relies on the ability to prepare kinetically stable, geometrically pure *fac* or *mer* tris-chelate sub-components as starting points to propagate a specific assembly.

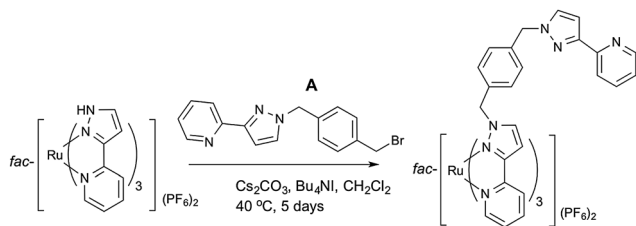
We report here the use of this principle – *viz.* control of geometric isomerism at specific sites in a cage as a way of directing assembly – in the formation of an unusual [Ru₄Ag₆(L^{ph})₁₂]¹⁴⁺ mixed-metal cage which combines octahedral *fac* tris-chelate Ru(II) vertices and pseudo-tetrahedral Ag(I) bis-chelate edges in an adamantane-type cage structure having tetrahedral symmetry. The novelty lies both in the structure of the cage [a combination of three-connected and two-connected metal vertices based on Ru(II) and Ag(I) respectively], and in the use of the pre-formed, kinetically stable [Ru(L^{ph})₃]²⁺ units as purely the *fac* isomer to direct the course of the self-assembly.

As *fac*-[ML₃]²⁺ units from this family occur at specific sites in many of our cages,^{1c} we wished to start with *fac*-[Ru(L^{ph})₃]²⁺ in which the three pendant binding sites, where cage propagation occurs by coordination to additional metal ions, have a *fac* arrangement. Simple reaction of Ru(dmsO)₄Cl₂ with > 3 equivalents of L^{ph} afforded [Ru(L^{ph})₃]²⁺ as a 1 : 3 statistical mixture of *fac*:*mer* isomers as shown by the ¹H NMR spectrum in which every type of proton (*e.g.* coordinated pyridyl H^δ) occurred in four different environments in a 1 : 1 : 1 : 1 ratio. However column chromatography or HPLC under a range of conditions did not give a good separation of the geometric isomers.

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† Electronic supplementary information (ESI) available: Crystallographic data in CIF format; details of crystallographic data collections and refinements; selected bond distances for the structures; synthesis and characterisation of new complexes, including ¹H NMR, COSY and DOSY spectra; additional figures of the cage [(Ru(L^{ph})₃)₄Ag₆](PF₆)₁₄. CCDC 1013864 and 1013865. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc05421k





Scheme 1 Preparation of fac -[Ru(L^{Ph})₃][PF₆]₂.

We therefore went back a step in the synthesis, to fac -[Ru(PyPzH)₃]²⁺ [Scheme 1; PyPzH = 3-(2-pyridyl)pyrazole] which can be readily separated from the *mer* isomer using a method reported earlier.¹² In fac -[Ru(PyPzH)₃]²⁺ the three pyrazole rings, with their acidic NH protons, lie of course on the same face of the complex. Alkylation of these^{12a} with the bromomethyl compound **A** completed the formation of the L^{Ph} ligands coordinated to the metal centre at one end, to give fac -[Ru(L^{Ph})₃]²⁺ which was isolated as the hexafluorophosphate salt (see ESI[†]). The ¹H NMR spectrum showed 20 ¹H environments confirming the threefold symmetry with all three ligands equivalent. Notably the CH₂ protons close to the Ru(II) chiral centre are diastereotopic, giving a coupled pair of doublets at 5.5 and 4.8 ppm, whereas the CH₂ protons more remote from the Ru(II) centre give a singlet at 5.3 ppm (Fig. S3, ESI[†]). The crystal structure of the complex cation of fac -[Ru(L^{Ph})₃][PF₆]₂·acetone is shown in Fig. 1; (ESI[†]) it is clear how the three pendant pyrazolyl-pyridine arms are directed to the same face of the complex. The phenyl group of each pendant arm forms a π -stacking interaction with a coordinated pyrazolyl-pyridine group from another ligand, as we have observed in related complexes.

Ag(I) generally forms four-coordinate bis-chelate complexes with pyrazolyl-pyridine ligands of this type.¹³ On the basis that three pendant bidentate sites are available for coordination in fac -[Ru(L^{Ph})₃][PF₆]₂, we combined (ESI[†]) fac -[Ru(L^{Ph})₃][PF₆]₂ with 1.5 equivalents of AgPF₆ to maximise the likelihood of a structure forming that conforms to the principle of maximum site occupancy, with all metal ions coordinatively saturated and

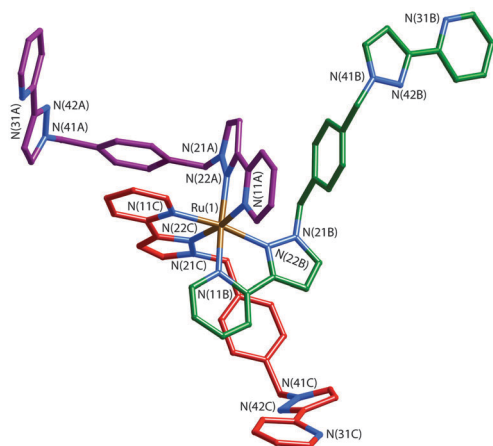


Fig. 1 Structure of the complex cation of fac -[Ru(L^{Ph})₃][PF₆]₂·acetone with the three ligands coloured differently for clarity.

all ligands fully coordinated.¹⁴ If each pendant ligand fragment coordinates to a different Ag(I) ion, as is likely on steric grounds given the distance between the pendant pyrazolyl-pyridine units, we expect a mixed-metal cage in which each fac -[Ru(L^{Ph})₃]²⁺ unit caps a triangular array of Ag(I) ions.

Slow crystallisation of the reaction mixture afforded X-ray quality crystals of what proved to be a decanuclear Ru₄Ag₆ cage [(Ru(L^{Ph})₃)₄Ag₆](PF₆)₁₄ (Fig. 2–4) (ESI[†]). The cage has an adamantane-like structure, with a Ru(II) tris-chelate unit at each of the four three-connected vertices which are arranged in an approximate tetrahedron. An Ag(I) bis-chelate unit occupies each of the six two-connected vertices. Thus the structure can be described as a tetrahedral array of Ru(II) ions with an Ag(I) ion lying in the centre of each Ru···Ru edge (Fig. 2), with every adjacent Ru(II)–Ag(I) pair connected by a bis-bidentate bridging ligand L^{Ph}.

The molecule lies astride a crystallographic C₂ axis such that half of it is unique. This axis passes through Ag(2) and Ag(3) such that these lie on special positions with 50% occupancy in the asymmetric unit, whereas Ag(1) and Ag(4) are in general positions. There is a (non-crystallographic) C₃ axis through each Ru(II) tris-chelate vertex, with all four being homochiral; thus the complex belongs to the pure rotation symmetry point group *T* which is a common consequence of removing mirror planes from high-symmetry polyhedra.

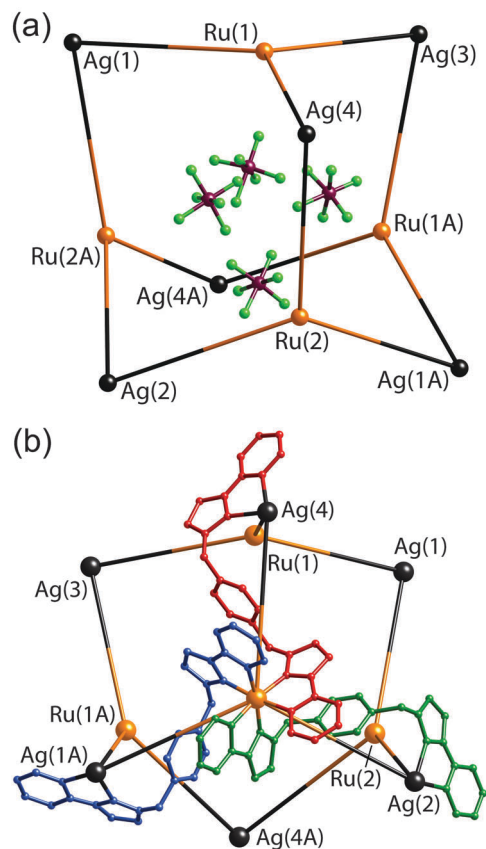


Fig. 2 Two views of the structure of [(Ru(L^{Ph})₃)₄Ag₆](PF₆)₁₄: (a) the adamantane-like arrangement of metal ions, with the four anions that lie within the cavity also shown; (b) the metal superstructure with three of the bridging ligands included (coloured differently for clarity).



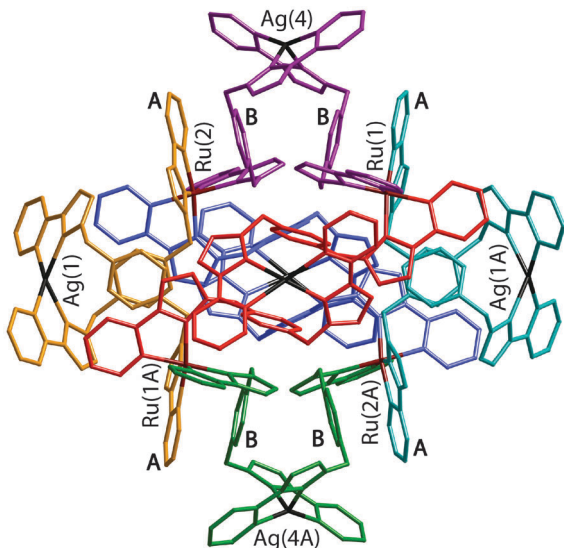


Fig. 3 A view of the complete complex cation of $\{[(Ru(L^{Ph})_3)_4Ag_6](PF_6)_{14}\}$. The two ligands coordinated to each Ag(i) have the same colour. Labels A and B denote the electron-deficient (pyrazolyl-pyridine) and electron-rich (phenyl) units involved in the pairwise π -stacking interactions.

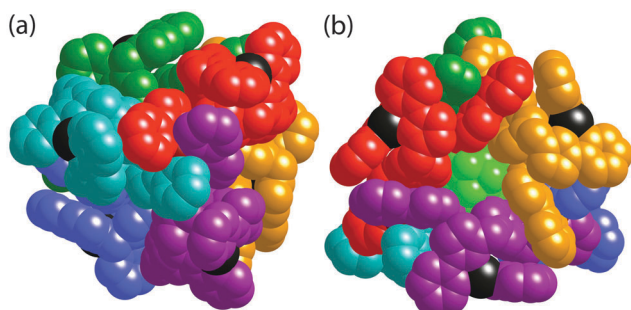


Fig. 4 Space-filling views of the complex cation of $\{[(Ru(L^{Ph})_3)_4Ag_6](PF_6)_{14}\}$. (a) A view down one of the threefold axes, through a Ru(II) tris-chelate centre; (b) a view from the opposite side of the complex looking at one of the Ru_3Ag_3 faces, with one of the encapsulated $[PF_6]^-$ anions (F atoms in green) visible through the portal.

The six Ag(i) ions lie on the three C_2 axes associated with T symmetry of which one [the Ag(2) \cdots Ag(3) axis, as mentioned above] occurs in the crystal structure; necessarily, all six Ag(i) ions have the same chirality associated with their two non-symmetrical chelating ligands. The nearest-neighbour Ru \cdots Ag separations (*i.e.* along an edge spanned by a bridging ligand) lie in the range 8.86–9.32 Å, averaging 9.06 Å.

The flexibility of the ligands associated with the CH_2 'hinges' allows them to adopt a conformation which maximises inter-ligand π -stacking – a key driver for assembly of such cages.^{16,15} This can be seen in the view shown in Fig. 3, in which the octahedral disposition of the six Ag(i) ions is emphasised with these being placed top/bottom, left/right and front/back with each pair of Ag(i) ions lying on a C_2 axis. In this view, Ag(4)/Ag(4A) form the 'vertical' C_2 axis. The two ligands attached to each Ag(i) ion have the same colour (*i.e.* the twelve ligands are coloured in six sets of two). The ligands

are disposed such that a central phenyl ring of a bridging ligand (denoted 'B' in Fig. 3) lies parallel to, and overlapping with, a pyrazolyl-pyridine unit of another ligand coordinated to the adjacent Ru(n) ion (denoted 'A' in Fig. 3), forming a charge-assisted π -stack between electron-rich (phenyl) and electron-deficient (coordinated pyrazolyl-pyridine) ligands. In the view in Fig. 3 we can readily see four such A/B stacked pairs; there are necessarily, therefore, twelve such interactions overall – involving every phenyl group – as the orientations with Ag(1)/Ag(1A) and Ag(2)/Ag(3) as the 'vertical' axis are equivalent.

An alternative space-filling view, looking down one of the C_3 axes associated with a Ru(n) tris-chelate centre, is in Fig. 4a. The cage complex has an approximate cavity size of 178 Å³ (calculated assuming that the windows are blocked; Fig. S2, ESI[†]). The cavity is occupied by a tetrahedral array of four $[PF_6]^-$ anions (Fig. 2a), each one blocking the window in one of the Ru_3Ag_3 faces of the cage, as shown in Fig. 4b in which three of the F atoms of the $[PF_6]^-$ anion in that window can be clearly seen. The P \cdots P separations between the four encapsulated anions are in the range of 5.44–5.61 Å, resulting in peripheral F \cdots F contacts between anions of \approx 3 Å, which is the sum of the van der Waals' radii of two F atoms. Each anion is involved in a range of CH \cdots F interactions with ligand H atoms. Fig. S1(a) (ESI[†]) shows one of the anions embedded in the window in one of the Ru_3Ag_3 faces, with dotted lines indicating some of the short non-bonded C \cdots F contacts (\leq 3.15 Å) which are indicative of weak hydrogen-bonding interactions between anion and ligand. This view also nicely shows how the array of six ligands around each Ru_3Ag_3 face forms a cyclic helicate with every ligand in the cycle having the same sense of 'under and over' around the ring. Fig. S1(b) (ESI[†]) shows how the four anions fill the cavity.

The structural integrity of the complex in solution was confirmed by ES mass spectrometry, which showed peaks corresponding to the species $\{[Ru_4Ag_6(L^{Ph})_{12}](PF_6)_{14-n}\}^{n+}$ ($n = 3, 4, 6$), and also by ¹H NMR spectroscopy (ESI[†]). The ¹H NMR spectrum at room temperature is very broad, indicative of molecular motions [possibly associated with the highly flexible Ag(i) centres] at a rate comparable to the ¹H NMR timescale. However at 75 °C the spectrum sharpened satisfactorily and showed the expected 20 independent ¹H signals associated with one environment for L^{Ph} with no internal symmetry (Fig. S6, ESI[†]); this spectrum is considerably different from that of *fac*- $[Ru(L^{Ph})_3](PF_6)_2$. Significantly, the chirality associated with the $\{Ag(NN)_2\}^+$ centres ensures that *both* independent sets of CH_2 protons are now diastereotopic, giving two pairs of coupled doublets in the 4.5–5.5 ppm region (Fig. S5, ESI[†]). That this species is a large assembly is confirmed by its DOSY spectrum which clearly shows that all of its ¹H signals belong to a single species which has a much lower diffusion rate [$\log D$ ($m^2 s^{-1}$) = -9.2] than *fac*- $[Ru(L^{Ph})_3](PF_6)_2$ [$\log D$ ($m^2 s^{-1}$) = -8.4] (Fig. S7, ESI[†]).

Assembly of this cage with its adamantane-like structure thus relies on two different types of geometric control at specific metal sites. Firstly it requires the appropriate combination of metal vertices that are three-connected [each tris-chelate, Ru(n) ion is connected to three Ag(i) ions] and two connected [each bis-chelate Ag(i) ion is connected to two Ru(n) ions]. This is achieved by using metal ions with different stereoelectronic preference, *i.e.* a combination of



6-coordinate Ru(II) and 4-coordinate Ag(I) ions at alternating sites. Secondly, the structure relies on exclusive use of pre-formed, kinetically inert *fac* isomers of the $[\text{Ru}(\text{L}^{\text{ph}})_3]^{2+}$ unit. We note that there are a few other examples of mixed-metal $\text{M}_6\text{M}'_4(\mu\text{-L})_{10}$ complexes with an adamantane-like core structure.^{16,17} Many of these arise from one-pot reactions, but some – which use cyanide bridges along the M–M' edges – are based on a kinetically stable, pre-formed hexacyanometallate unit as one precursor in a manner related to ours.¹⁷ In principle the method we have reported here should have high generality as it could be extended to other kinetically inert octahedral d^6 metal complexes of the type *fac*- $[\text{M}(\text{PyPzH})_3]^{n+}$ (M = Os, $n = 2$; M = Rh, Ir, $n = 3$ etc.).

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