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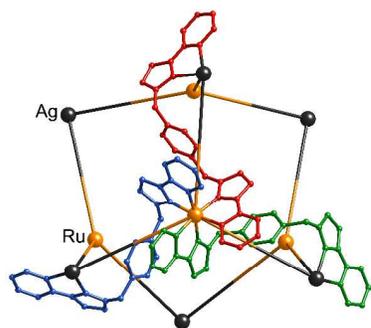
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# Stepwise assembly of an adamantoid $\text{Ru}_4\text{Ag}_6$ cage by control of metal coordination geometry at specific sites

Alexander J. Metherell and Michael D. Ward\*

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A Ru(II) tris-chelate complex with three pendant binding sites on the same face combines with Ag(I) to form a  $\text{Ru}_4\text{Ag}_6$  cage



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ARTICLE TYPE

# Stepwise assembly of an adamantoid $\text{Ru}_4\text{Ag}_6$ cage by control of metal coordination geometry at specific sites

Alexander J. Metherell and Michael D. Ward\*

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The geometrically pure 'complex ligand'  $\text{fac}[\text{Ru}(\text{L}^{\text{ph}})_3]^{2+}$ , in which three pendant bidentate binding sites are located on one face of the complex, reacts with  $\text{Ag}(\text{I})$  ions to form the adamantoid decanuclear cage  $[\{\text{Ru}(\text{L}^{\text{ph}})_3\}_4\text{Ag}_6](\text{PF}_6)_{14}$  which contains a 6-coordinate  $\text{Ru}(\text{II})$  ion at each vertex of a large tetrahedron and a 4-coordinate  $\text{Ag}(\text{I})$  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.<sup>1</sup> In addition the ability of cages to bind guest molecules in their central cavity leads to potential applications<sup>2</sup> ranging from catalysis<sup>3</sup> to drug delivery.<sup>4</sup>

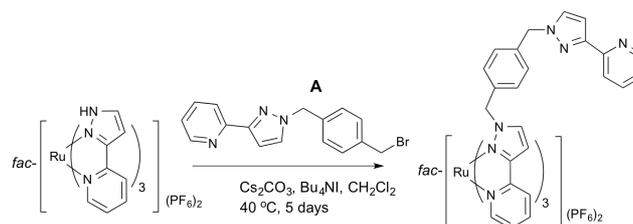
The vast majority of cages are formed from just two types of component: one type of metal ion and one type of ligand. A few examples of mixed-ligand cages are known in which the self assembly process specifically occurs with selection of two different types of ligand, resulting in a heteroleptic complex being favoured over the homoleptic alternatives.<sup>5</sup> 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.<sup>6-8</sup> 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.<sup>7</sup> 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.<sup>8</sup>

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.<sup>1c</sup> 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  $\text{M}_4\text{L}_6$  tetrahedra, all four metal centres have a *fac* tris-chelate geometry,<sup>9</sup> in contrast, in a series of  $\text{M}_{12}\text{L}_{18}$  truncated tetrahedra, all metal centres have a *mer* tris-chelate geometry.<sup>10</sup> In several other types of cage assembly however there is a 3:1 mixture of *mer* : *fac* tris-chelate vertices.<sup>11</sup>

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 subcomponents as starting points to propagate a specific assembly.

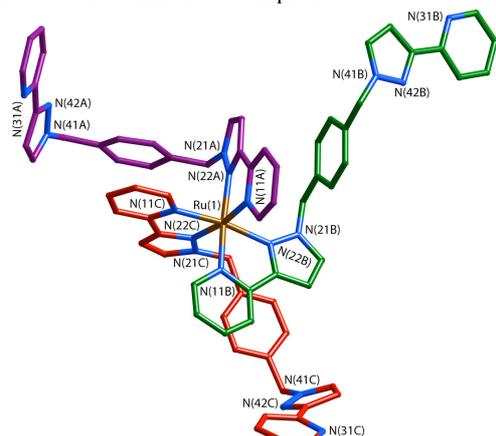
We report here the use of this principle – *viz.* control of geometric isomerism at specific sites in a cage as a way of directing assembly – in the formation of an unusual  $[\text{Ru}_4\text{Ag}_6(\text{L}^{\text{ph}})_{12}]^{14+}$  mixed-metal cage which combines octahedral *fac* tris-chelate  $\text{Ru}(\text{II})$  vertices and pseudo-tetrahedral  $\text{Ag}(\text{I})$  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  $\text{Ru}(\text{II})$  and  $\text{Ag}(\text{I})$  respectively], and in the use of the pre-formed, kinetically stable  $[\text{Ru}(\text{L}^{\text{ph}})_3]^{2+}$  units as purely the *fac* isomer to direct the course of the self-assembly.

As *fac*- $[\text{ML}_3]^{2+}$  units from this family occur at specific sites in many of our cages,<sup>1c</sup> we wished to start with *fac*- $[\text{Ru}(\text{L}^{\text{ph}})_3]^{2+}$  in which the three pendant binding sites, where cage propagation occurs by coordination to additional metal ions, have a *fac* arrangement. Simple reaction of  $\text{Ru}(\text{dmsO})_4\text{Cl}_2$  with > 3 equivalents of  $\text{L}^{\text{ph}}$  afforded  $[\text{Ru}(\text{L}^{\text{ph}})_3]^{2+}$  as a 1:3 statistical mixture of *fac*:*mer* isomers as shown by the <sup>1</sup>H NMR spectrum in which every type of proton (*e.g.* coordinated pyridyl H<sup>δ</sup>) 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.

Scheme 1. Preparation of *fac*- $[\text{Ru}(\text{L}^{\text{ph}})_3][\text{PF}_6]_2$ 

We therefore went back a step in the synthesis, to *fac*- $[\text{Ru}(\text{PyPzH})_3]^{2+}$  [Scheme 1;  $\text{PyPzH} = 3\text{-(2-pyridyl-pyrazole)}$ ] which can be readily separated from the *mer* isomer using a method reported earlier.<sup>12</sup> In *fac*- $[\text{Ru}(\text{PyPzH})_3]^{2+}$  the three pyrazole rings, with their acidic NH protons, lie of course on the same face of the complex. Alkylation of these<sup>12a</sup> with the bromomethyl compound **A** completed the formation of the  $\text{L}^{\text{ph}}$

ligands coordinated to the metal centre at one end, to give *fac*-[Ru(L<sup>ph</sup>)<sub>3</sub>]<sup>2+</sup> which was isolated as the hexafluorophosphate salt (see ESI).<sup>†</sup> The <sup>1</sup>H NMR spectrum showed 20 <sup>1</sup>H environments confirming the threefold symmetry with all three ligands equivalent. Notably the CH<sub>2</sub> 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 CH<sub>2</sub> protons more remote from the Ru(II) centre give a singlet at 5.3 ppm (Fig. S3).<sup>†</sup> The crystal structure of the complex cation of *fac*-[Ru(L<sup>ph</sup>)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub>•acetone is shown in Fig. 1;<sup>†</sup> 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  $\pi$ -stacking interaction with a coordinated pyrazolyl-pyridine group from another ligand, as we have observed in related complexes.



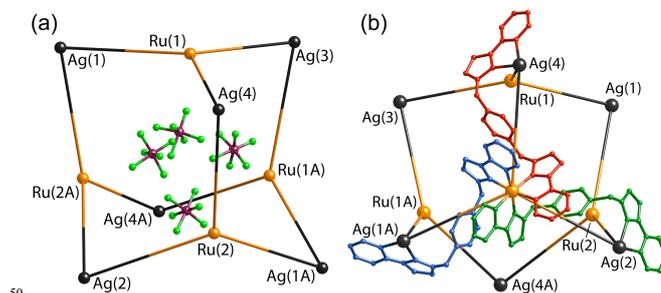
**Fig. 1.** Structure of the complex cation of *fac*-[Ru(L<sup>ph</sup>)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub>•acetone with the three ligands coloured differently for clarity.

Ag(I) generally forms four-coordinate bis-chelate complexes with pyrazolyl-pyridine ligands of this type.<sup>13</sup> On the basis that three pendant bidentate sites are available for coordination in *fac*-[Ru(L<sup>ph</sup>)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub>, we combined *fac*-[Ru(L<sup>ph</sup>)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub> with 1.5 equivalents of AgPF<sub>6</sub> to maximise the likelihood of a structure forming that conforms to the principle of maximum site occupancy, with all metal ions coordinatively saturated and all ligands fully coordinated.<sup>14</sup> 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<sup>ph</sup>)<sub>3</sub>]<sup>2+</sup> unit caps a triangular array of Ag(I) ions.

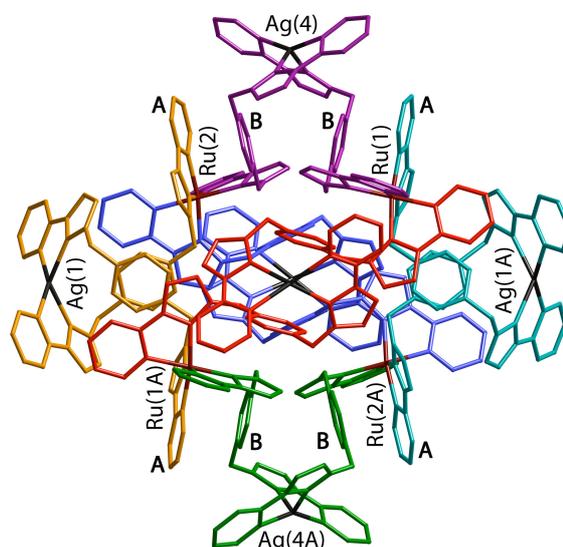
Slow crystallisation of the reaction mixture afforded X-ray quality crystals of what proved to be a decanuclear Ru<sub>4</sub>Ag<sub>6</sub> cage [ $\{Ru(L^{ph})_3\}_4Ag_6\}(PF_6)_{14}$ ] (Fig. 2 – 4).<sup>†</sup> The cage has an adamantane-like structure, with a Ru(II) tris-chelate unit at each of the 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<sup>ph</sup>.

The molecule lies astride a crystallographic C<sub>2</sub> 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) C<sub>3</sub> 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 [ $\{Ru(L^{ph})_3\}_4Ag_6\}(PF_6)_{14}$ ]: (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).

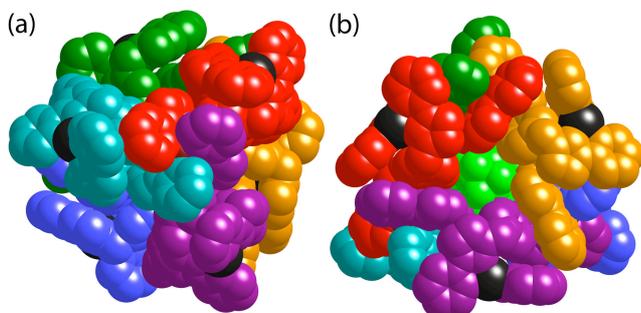


**Fig. 3.** A view of the complete complex cation of [ $\{Ru(L^{ph})_3\}_4Ag_6\}(PF_6)_{14}$ ]. The two ligands coordinated to each Ag(I) have the same colour. Labels A and B denote the electron-deficient (pyrazolyl-pyridine) and electron-rich (phenyl) units involved in the pairwise  $\pi$ -stacking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

The six Ag(I) ions lie on the three C<sub>2</sub> axes associated with T symmetry of which one [the Ag(2)•••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•••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<sub>2</sub> ‘hinges’ allows them to adopt a conformation which maximises inter-ligand  $\pi$ -stacking – a key driver for assembly of such cages.<sup>16,15</sup> 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<sub>2</sub> axis. In this view, Ag(4)/Ag(4A) form the ‘vertical’ C<sub>2</sub> 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(II) ion (denoted 'A' in Fig. 3), forming a charge-assisted  $\pi$ -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.



**Fig. 4.** Space-filling views of the complex cation of  $[\{\text{Ru}(\text{L}^{\text{ph}})_3\}_4\text{Ag}_6](\text{PF}_6)_4$ . (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  $\text{Ru}_3\text{Ag}_3$  faces, with one of the encapsulated  $[\text{PF}_6]^-$  anions (F atoms in green) visible through the portal.

An alternative space-filling view, looking down one of the  $C_3$  axes associated with a Ru(II) tris-chelate centre, is in Fig. 4a. The cage complex has an approximate cavity size of  $178 \text{ \AA}^3$  (calculated assuming that the windows are blocked; Fig. S2).<sup>†</sup> The cavity is occupied by a tetrahedral array of four  $[\text{PF}_6]^-$  anions (Fig. 2a), each one blocking the window in one of the  $\text{Ru}_3\text{Ag}_3$  faces of the cage, as shown in Fig. 4b in which three of the F atoms of the  $[\text{PF}_6]^-$  anion in that window can be clearly seen. The  $\text{P}\cdots\text{P}$  separations between the four encapsulated anions are in the range of  $5.44 - 5.61 \text{ \AA}$ , resulting in peripheral  $\text{F}\cdots\text{F}$  contacts between anions of  $\approx 3 \text{ \AA}$ , which is the sum of the van der Waals' radii of two F atoms. Each anion is involved in a range of  $\text{C}\cdots\text{F}$  interactions with ligand H atoms. Fig. S1(a)<sup>†</sup> shows one of the anions embedded in the window in one of the  $\text{Ru}_3\text{Ag}_3$  faces, with dotted lines indicating some of the short non-bonded  $\text{C}\cdots\text{F}$  contacts ( $\leq 3.15 \text{ \AA}$ ) 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  $\text{Ru}_3\text{Ag}_3$  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)<sup>†</sup> 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  $[\{\text{Ru}_4\text{Ag}_6(\text{L}^{\text{ph}})_{12}\}(\text{PF}_6)_{14-n}]^{n+}$  ( $n = 3, 4, 6$ ), and also by  $^1\text{H}$  NMR spectroscopy.<sup>†</sup> The  $^1\text{H}$  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  $^1\text{H}$  NMR timescale. However at  $75^\circ\text{C}$  the spectrum sharpened satisfactorily and showed the expected 20 independent  $^1\text{H}$  signals associated with one environment for  $\text{L}^{\text{ph}}$  with no internal symmetry (Fig. S6).<sup>†</sup>

this spectrum is considerably different from that of *fac*- $[\text{Ru}(\text{L}^{\text{ph}})_3](\text{PF}_6)_2$ . Significantly, the chirality associated with the  $\{\text{Ag}(\text{NN})_2\}^+$  centres ensures that *both* independent sets of  $\text{CH}_2$  protons are now diastereotopic, giving two pairs of coupled doublets in the  $4.5 - 5.5 \text{ ppm}$  region (Fig. S5).<sup>†</sup> That this species is a large assembly is confirmed by its DOSY spectrum which clearly shows that all of its  $^1\text{H}$  signals belong to a single species which has a much lower diffusion rate [ $\log D(\text{m}^2 \text{ s}^{-1}) = -9.2$ ] than *fac*- $[\text{Ru}(\text{L}^{\text{ph}})_3](\text{PF}_6)_2$  [ $\log D(\text{m}^2 \text{ s}^{-1}) = -8.4$ ] (Fig. S7).<sup>†</sup>

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(II) ion is connected to three Ag(I) ions] and two connected [each bis-chelate Ag(I) ion is connected to two Ru(II) 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.<sup>16,17</sup> Many of these arise from one-pot reactions, but some – which use cyanide bridges along the  $\text{M}-\text{M}'$  edges – are based on a kinetically stable, pre-formed hexacyanometallate unit as one precursor in a manner related to ours.<sup>17</sup> 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*- $[\text{M}(\text{PyPzH})_3]^{n+}$  ( $\text{M} = \text{Os}, n = 2; \text{M} = \text{Rh}, \text{Ir}, n = 3 \text{ etc.}$ ).

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## Notes and references

Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK, E-mail: m.d.ward@sheffield.ac.uk

<sup>†</sup> 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  $^1\text{H}$  NMR, COSY and DOSY spectra; additional figures of the cage  $[\{\text{Ru}(\text{L}^{\text{ph}})_3\}_4\text{Ag}_6](\text{PF}_6)_4$ . CCDC 1013864 and 1013865. See DOI: 10.1039/b000000x/

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