

Self-assembly of a twelve-component hexanuclear metallomacrocyclic constructed with a novel tri-amino ligand†

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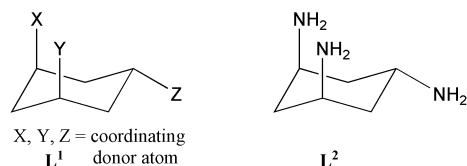
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Reaction of the novel ligand *cis,trans*-1,3,5-triaminocyclohexane, which contains two types of metal binding sites *trans* to each other, with palladium(II) chloride results in the self assembly of a hexanuclear ring cluster that has been characterised both in the solid state and in solution.

It is now well established that supramolecular self-assembly through metal coordination has shown remarkable potential for the construction of well-defined architectures through both serendipity¹ and design.² Such structures include an array of two dimensional systems, such as rhomboids, squares, pentagons and hexagons as well as three dimensional systems, such as truncated tetrahedra, adamantoids, cuboctahedra, dodecahedra and a wide variety of other systems.^{1,3–6} It is remarkable that many of these systems can now be synthesised by programmed design; one such strategy is achieved by choosing a building block where the number of kinetically inert and labile sites are controlled. For example a building block comprising a Pd(II) or Pt(II) ion can have two of the four square planar coordination sites effectively ‘blocked’ by amino or phosphino ligands. When the ligands are *cis* chelating ligands the building block can be used as a corner unit in the assembly of a molecular square or related structures, as exemplified by the work of Fujita^{2,3} and Stang.^{4,5} The spacer groups are nearly always of the bipyridyl or pyrazolyl type as it appears that these allow a greater degree of kinetic reversibility to allow the formation of a given supramolecular architecture.²

We are currently investigating the coordination chemistry of tri-substituted *cis,trans*-cyclohexanes (**L**¹), and topologically related derivatives, as potential new building blocks for the assembly of supramolecular architectures. The novelty of this type of ligand is that it can provide two types of coordination environments which appear to combine the two types of building blocks often exploited in the assembly of metal-supramolecular architectures; a chelating blocking unit and a mono-coordinating unit as a spacer. In this study we have concentrated on the ligand, *cis,trans*-1,3,5-triaminocyclohexane, (*trans*-tach or **L**²),⁷ and we present the first structurally characterised complex of this novel ligand that demonstrates its potential as a new type of building block.⁸



The reaction of **L**²·3HCl with 1.5 equivalents of PdCl₂ under reflux, followed by neutralisation of the solution and reduction of volume results in the crystallisation of the hexanuclear palladium(II) cluster **1** in a 30% yield (see ESI for experimental

details†). In the formation of this cluster **1**, both the *cis*-bidentate amino moiety and the *trans* amino moiety of the ligand **L**² are utilised to form a hexanuclear cluster with a circular topology of the form [Pd₆(**L**²)₆Cl₆]Cl₆ (**1**) which has been structurally characterised by single crystal X-ray crystallography,§ see Fig. 1. The asymmetric unit comprises three crystallographically independent {Pd(**L**²)Cl} units. A crystallographic inversion centre lies between the two coordinated chloro ligands that point towards the centre of the cavity (Cl3 and Cl3*), see Fig. 1.

The palladium(II) ions adopt a pseudo compressed chair conformation with the closest Pd...Pd distance being 5.19 Å (Pd2...Pd3*) and the furthest Pd...Pd distance being 13.72 Å (Pd1...Pd1*). Each palladium(II) ion adopts a square planar geometry with the chelate coordination of two *cis* amino ‘head’ groups [2.035(6) ≤ d(Pd–N) ≤ 2.065(5) Å] from one *trans*-tach ligand and coordination of the *trans* amino ‘tail’ nitrogen from another *trans*-tach ligand [2.064(5) ≤ d(Pd–N) ≤ 2.071(5) Å]. The coordination sphere is completed by a chloro ligand [2.292(2) ≤ d(Pd–Cl) ≤ 2.316(2) Å]. The cluster was also confirmed to be present in solution by ¹H-NMR spectroscopy. Features related to the cyclohexane backbone are shown in Fig.

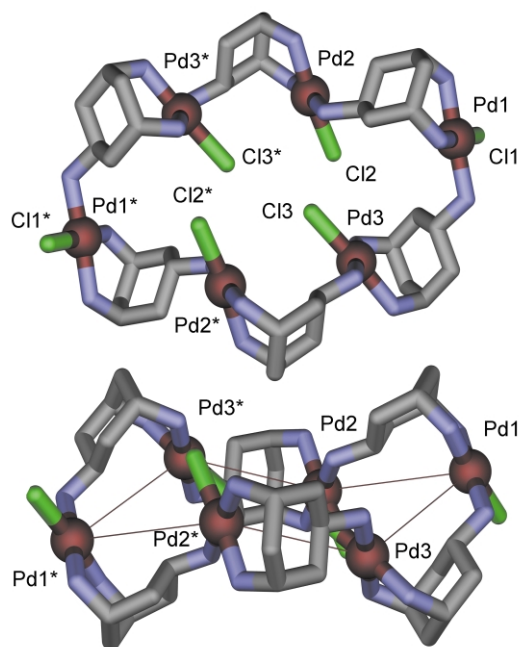


Fig. 1 Representations of the X-ray crystal structure of the hexanuclear palladium cluster, [Pd₆(**L**²)₆Cl₆]⁶⁺ (**1**). A top view is shown (top) and a side view (bottom). The palladium(II) ions are shown as the dark red spheres, the chloro ligands in green, the nitrogen atoms in blue and the carbon atoms in dark grey. The two coordination environments exhibited by the tach ligand (**L**²) can be clearly seen as can the overall circular topology of the complex. The bottom view shows the palladium(II) ions linked by a thin line to highlight the pseudo chair conformation of the palladium(II) ions relative to each other. The remaining six chloride ions and water molecules are omitted.

† Electronic supplementary information (ESI) available: experimental details. See <http://www.rsc.org/suppdata/cc/b2/b209493m/>

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2 and were de-convoluted by 2D NMR studies (see ESI[†]) and can be successively assigned. Of particular note are the peaks labelled Ha, Hb, Hc which each integrate to one proton of the total number of 27 (CH)_n protons in the spectrum and can be tentatively assigned[§] as methine protons (R₂(CH)NH₂) in the axial positions of the cyclohexane rings.⁹

These three resonances imply the presence of three chemically different cyclohexane rings in solution and are consistent with the solid state crystal structure which comprises six *trans*-tach ligands and an inversion centre, see Fig. 3.

Therefore, it can be suggested, on the basis of the structural evidence and previous precedents,^{9–11} that Ha is most deshielded due to its close contacts with Pd2* (Ha...Pd2* = 2.47 Å, C2*–Ha–Pd2* = 133.1°) and also with Cl3 (Ha...Cl3 = 2.88 Å, Pd3–Cl3–Ha = 71.3°) on the adjacent cyclohexane ring. Hb is less deshielded, also making a close contact with Pd3 (Hb...Pd3 = 2.47 Å, C3–Hb–Pd3 = 131.4°), but has no close contacts with any chloro ligands. Hc is least deshielded, making only contact with Pd1* (Hc...Pd1* = 2.75 Å, C1*–Hc–Pd1* = 127.4°) with a significantly longer Pd...H distance (2.75 Å) than Ha or Hb, see Fig. 3. The identity of Hb is further confirmed by its *trans* coupling to Hd, see Fig. 4.

Hd is also deshielded from the bulk methylene protons and integrates to 1/27th of the total number of protons. Analysis of the crystal structure confirms that Hd is the only methylene proton in the asymmetric unit that is in close contact with a chloro ligand (Hd...Cl1 = 3.04 Å, Pd1–Cl1–Hd = 81.4°) see Figs. 3 and 4, supporting our assignments.

The close contacts of Ha and Hd with the chloro ligands could be referred to as hydrogen-bonded interactions,¹⁰ as could the Pd...H(a,b,c)–C interactions; but given the built in geometrical restrictions of the ligand–metal complex, these interactions are difficult to quantify.¹¹ However, the correlation between the NMR and the crystal data appears quite remarkable and implies that one can differentiate between the three different *trans*-tach units of the ring. Variable temperature NMR experiments have shown that the spectrum remains unchanged up to 65 °C and these results, therefore, indicate that the cluster is very rigid. However, increasing the temperature to 90 °C results in the decomposition of the cluster.[§] Such rigidity is probably attributable to the two 'endo' chloro ligands (Cl3/Cl3*) which

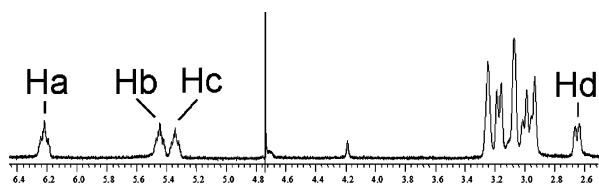


Fig. 2 A section of the ¹H-NMR spectrum recorded for **1** in D₂O.

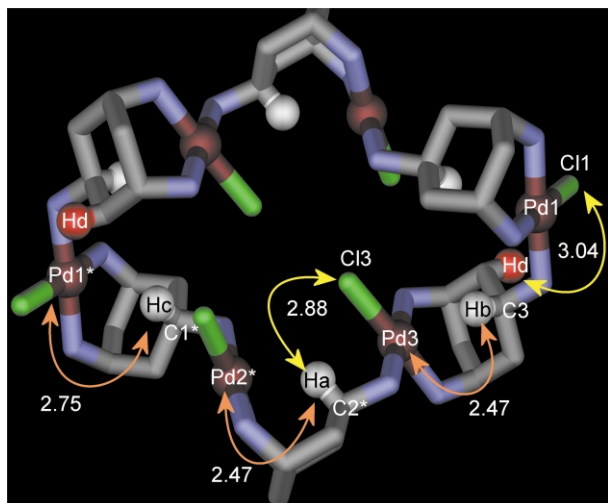


Fig. 3 A representation of the structure of **1** with the distances (in Å) between the axial methine protons and its adjacent Pd(n) and Cl ions, shown in orange and yellow respectively.

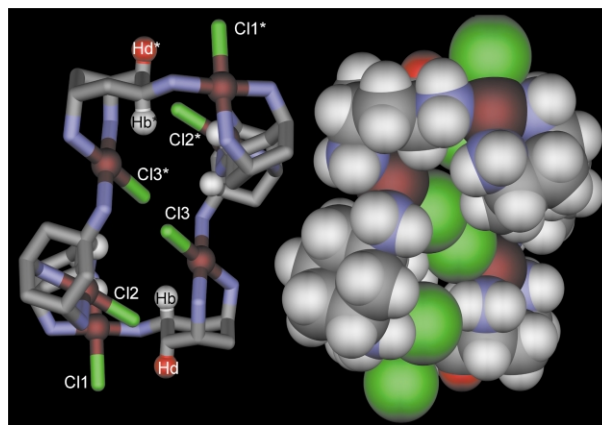


Fig. 4 LHS: a stick representation of the cluster showing the two 'exo' chloro ligands (Cl1/Cl1*) and the two 'endo' chloro ligands (Cl3/Cl3*) which have positions intermediate between the *endo* and *exo* chloro ligands. Both sets of protons Hb/Hb* and Hd/Hd* are shown in white and red respectively; the *trans* relationship between Hb and Hd can be clearly seen. RHS: a CPK representation of the cluster shows how both the 'endo' chloro ligands fill the cavity and the 'exo' chloro ligands protrude from the cavity.

'fill' the cavity and the two 'exo' chloro ligands (Cl1/Cl1*) which protrude from the cavity along with the two remaining chloro ligands (Cl2/Cl2*) which have positions intermediate between the *endo* and *exo* chloro ligands. Therefore it would appear that these chloro ligands 'lock' the geometry of the ring; this can be seen by examining the CPK model of the ring; see Fig. 4.

In conclusion, the bi-modal coordination ability of *cis,trans*-1,3,5-triaminocyclohexane (**L**²) with bidentate ('head', *cis*) and monodentate ('tail', *trans*) coordinating moieties has been demonstrated. Furthermore, combination of these two building blocks in one ligand facilitates the formation of a metal-lomacrocyclic. Further studies will examine the possibility of anion exchange in the assembly of similar architectures and the consequences of the *cis,trans* displacement of two non-equivalent binding sites, as contained in our ligand **L**² and derivatives of **L**¹. This work will be extended to other systems involving other metals and derivatives of our interesting ligand. We would like to thank Dr N. Spencer for his collaboration and the Universities of Birmingham and Glasgow for funding.

Notes and references

§ Full synthetic and analytical details are given in the ESI.[†] Crystal data for **1**: (C₃₆H₃₀Cl₂N₁₈Pd₆)·11.56H₂O, *M* = 2047.32, triclinic, space group *P* $\bar{1}$, *a* = 11.924(2), *b* = 12.710(3), *c* = 13.929(3) Å, α = 79.12(3), β = 68.93(3), γ = 88.33(3)°, *V* = 1932.7(7) Å³, *Z* = 1, μ (Mo–K α) = 1.837 mm^{−1}, 15688 reflections measured, 8782 unique which were used in all calculations. Final *R*₁ = 0.061 and *wR*₂ = 0.140 (all data). Structure solution with SHELXS97 and refinement with SHELXL97 via WinGX.¹² Hydrogen atom positions calculated and subsequently riding. CCDC 184116. See <http://www.rsc.org/suppdata/cc/b2/b209493m/> for crystallographic data in CIF or other electronic format.

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