Self-assembly and X-ray structure of a ten-component, three-dimensional metallosupramolecular cage

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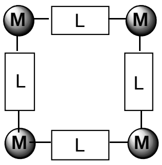
Reaction of 1,3,5-tris(pyrazol-1-ylmethyl)-2,4,6-triethylbenzene 7 with palladium chloride results in the self-assembly of a three-dimensional cage; an X-ray crystal structure determination shows that the cage is comprised of an octahedral arrangement of six palladium atoms bridged by a tetrahedral network of four molecules of the ligand and contains a (disordered) guest molecule of dimethyl sulfoxide.

The use of metal ions to control the self-assembly of multicomponent supramolecular structures of varying architecture is a subject of much current investigation;[1] particular recent attention has focused on the formation of species with internal cavities.[2] Since 1990, several groups have reported the construction of various molecular squares, represented schematically by structure **1**.[3] Lehn and coworkers[4] subsequently reported the formation of a three-dimensional cylindrical molecular box **2**, comprised of six metal ions and two types of bridging ligand. Fujita *et al.* have since reported the assembly of a five-component molecular cage[5] and, most recently, a ten-component adamantanoid-type cage **3** comprised of six metals with four identical bridging ligands.[6] We now report the formation and X-ray structure of a constitutionally similar but topologically different M$_6$L$_4$ cage.

We are currently engaged in a detailed study[7] of the coordination chemistry of a series of polyheteroaryl-substituted arenes **4**, which consist of various heterocyclic rings attached *via* spacer groups, X, to a central arene core, and have reported the syntheses of a number of poly(pyrazolylmethyl)benzenes.[8] We have also shown that the mesitylene-derived ligands **5** and **6** are able to encapsulate an octahedral metal atom, with simultaneous η^6-arene coordination and tripodal chelation to the pyrazole rings.[9] We have now extented this study to examine the complexes of these ligands with metal ions of different coordination geometry. In an effort to pre-organise the three pyrazole rings on the same side of the benzene ring,[10] we have now synthesised the triethyl analogue **7**, by trisbromomethylation[11] of 1,3,5-triethylbenzene, and subsequent phase-transfer-catalysed reaction with pyrazole.†

Reaction of **7** with palladium chloride gave immediate precipitation of an orange product,‡ which, on dissolution in Me$_2$SO, gave a ^{1}H NMR spectrum that showed significantly different chemical shifts from those of **7**, but retained the threefold symmetry. This was difficult to explain in terms of a square-planar palladium complex of low-nuclearity. Single crystals of this compound were grown by diffusion of acetone into an Me$_2$SO solution of the solid, but these decomposed instantaneously upon removal of the solvent. After many attempts, a crystal was successfully tranferred to the low-temperature stream of a four-circle diffractometer with only minor decomposition.§

Fig. 1 shows a perspective view of the major component of the contents of the asymmetric unit of this structure.¶ It consists of a ten-component, three-dimensional metallosupramolecular cage comprised of six *trans*-dichloropalladium units bridged by four molecules of **7**. The six palladium atoms are arranged in a pseudo-octahedral array, while the four molecules of **7** form a tetrahedrally disposed internal core of benzene rings of approximately 4.7 Å internal radius. Within this core resides a single (disordered) Me$_2$SO molecule (not shown in Fig.1). The potential T_d symmetry is not crystallographically imposed, and is destroyed by differing conformations of the ethyl groups; specifically, one of the ligands has all three terminal methyl groups directed towards the internal core, while the other three ligands have one methyl group directed outside the core. This, along with the presence of the Me$_2$SO guest and intermolecular interactions, results in a significant reduction in symmetry



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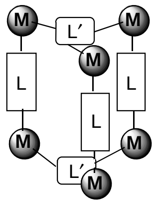

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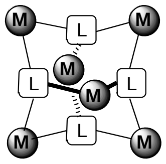

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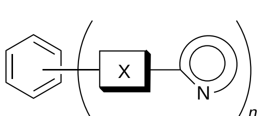

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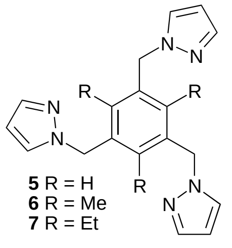

5 R = H
6 R = Me
7 R = Et

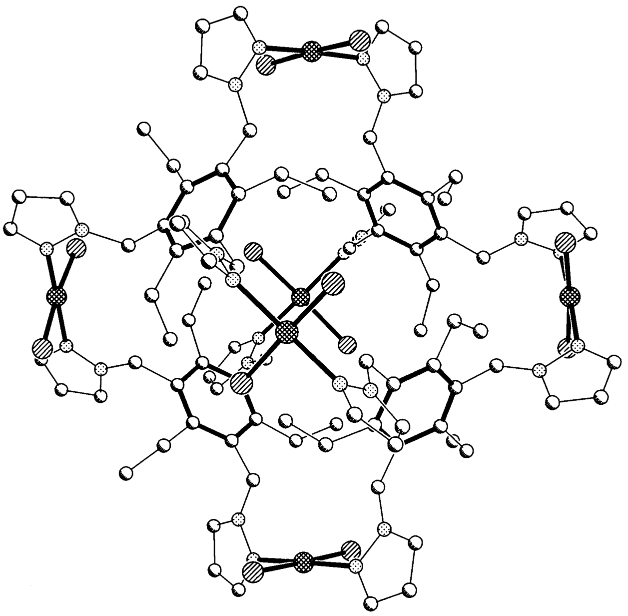

Fig. 1. Perspective view of the X-ray crystal structure; hydrogen atoms and solvate molecules not shown for clarity

in the solid state. For example, the diagonally opposite palladium atoms have separations ranging from 13.26 to 15.54 Å (Fig. 2). We believe that this cage structure is maintained in solution, which explains the symmetry observed in the NMR spectra and the slight broadening of the signals due to the methyl and methylene protons.

This molecule represents the second example of a M_6L_4 supramolecular adamantanoid cage, and serves to demonstrate the generality of such assembly processes; examples are also known of stoichiometrically inverted M_4L_6 compounds.[12] It is also the first X-ray structure of a free cage of this sort; in the previous example,[6] a low-precision X-ray structure of a clathrate complex with four adamantanyl carboxylate ions was determined. Although constitutionally similar to the previously reported M_6L_4 cage, the present structure is topologically quite different in shape. This is primarily a consequence of the different coordination geometries of the palladium atoms in the two compounds. In the only other example,[6] the bridging ligands were obligatorily *cis*-coordinated to the palladiums, due to the presence of chelating ethylenediamine ancillary ligands; in the present case, the ligands are *trans*- coordinated, which has the effect of making the palladiums more exposed on the surface of the cage. Furthermore, the methylene spacer groups in **7** impart greater flexibility to the ligand and, combined with the fact that the coordinating nitrogen is adjacent to the spacer group, allows for more compact packing within the cage; in the earlier case[6] the diagonally opposite palladiums were separated by *ca.* 19 Å.

The internal core of four tetrahedrally arranged benzene rings is reminiscent of that in the recently synthesised $C_{36}H_{36}$ spheriphane molecule which has covalently bonded ethylene bridges linking the benzenes and a radius of the internal cavity (as measured from the centroids of the rings) of 2.84 Å.[13] In the present case, the nature of the bridges expands this core to a radius of approximately 4.7 Å and allows for the incorporation of an Me_2SO guest molecule. The octahedral arrangement of the six metals is also related to that in the hexacoordinated palladium and platinum complexes of C_{60}, wherein the diagonally opposite metals are separated by *ca.* 11.2 Å and the internal core has a diameter of only 3.51 Å.[14]

In conclusion, we have shown that, upon reaction with palladium chloride, the ligand **7** self-assembles into a ten-component metallosupramolecular cage. Studies directed towards the assembly of related structures employing other bridging ligands, including dissymmetric and asymmetric examples, are currently in progress.

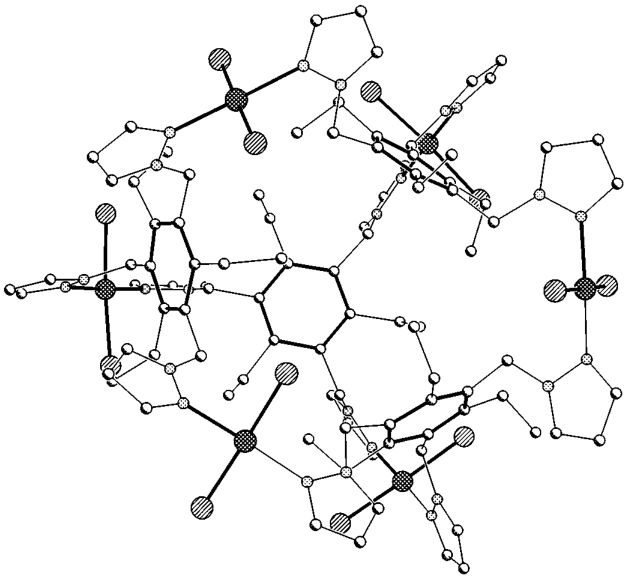

Fig. 2. View perpendicular to one benzene ring showing the reduction from T_d symmetry, in the solid state

Footnotes

† *Selected data* for **7**: isolated yield 60%, mp 125–126 °C (light petroleum). Found: C, 71.89; H, 7.73; N, 20.69. $C_{24}H_{30}N_6$ requires C, 71.61; H, 7.51; N, 20.88%. ^{1}H NMR ($CDCl_3$): δ 0.96 (9 H, t, CH_3), 2.70 (6 H, m, 2,4,6-CH_2), 5.45 (6 H, s, 1,3,5-CH_2), 6.20 (3 H, t, H 4′), 6.98 (3 H, d, H5′), 7.55 (3 H, d, H3′). ^{1}H NMR [$(CD_3)_2SO$]: δ 0.88 (9 H, t, CH_3), 2.88 (6 H, m, 2,4,6-CH_2), 5.47 (6 H, s, 1,3,5-CH_2), 6.32 (3 H, t, H4′), 7.53 (3 H, d, H5′), 7.57 (3 H, d, H3′).

‡ *Selected data*: isolated yield 87%, mp > 295 °C (decomp.) Found: C, 41.09; H, 4.92; N, 11.37; Cl, 14.93. $C_{96}H_{120}Cl_{12}N_{24}\ Pd_6\cdot 2C_2H_6OS\cdot 4H_2O$ requires C, 41.38; H, 4.86; N, 11.58; Cl, 14.66%. ^{1}H NMR [$(CH_3)_2SO$]: δ 1.23 (9 H, br t, CH_3), 2.50 (6 H, br m, 2,4,6-CH_2), 6.50 (6 H, br s, 1,3,5-CH_2), 6.65 (3 H, t, H4′), 7.93 (3 H, d, H5′), 8.15 (3 H, d, H3′).

§ *Crystal data* for $(PdCl_2)_6(\mathbf{7})_4\cdot 8Me_2SO\cdot 8H_2O$: $C_{112}H_{184}Cl_{12}N_{24}O_{16}Pd_6S_8$, $M_w = 3443.1$, triclinic, space group $P\bar{1}$, $a = 19.648(6)$, $b = 19.730(5)$, $c = 24.995(5)$ Å, $\alpha = 97.94(1)$, $\beta = 108.88(1)$, $\gamma = 95.17(2)$°, $U = 8986(4)$ Å^3, $Z = 2$, $D_c = 1.273$ g cm^{-3}, $\mu = 0.91$ mm^{-1}, $F(000) = 3520$, $T = -105$ °C. Cell parameters were determined by least-squares refinement of 35 accurately centred reflections. A yellow block (0.44 × 0.30 × 0.17 mm) was used to collect (Siemens P4s diffractometer, Mo-Kα radiation, ω scans) 21966 independent reflections with $4 < 2\theta < 44$°, with significant crystal decomposition during data collection. The structure was solved by a combination of Patterson and difference Fourier methods and refined on F^2, using all data, to $R = 0.0692$, $R_w = 0.1849$ for 1654 parameters.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/372.

¶ In addition to the atoms shown in Fig. 1, the asymmetric unit contains a Me_2SO guest in the cavity of the cage which has the sulfur atom disordered over two sites, and, external to the cage, seven Me_2SO and eight water solvate molecules, many of which are also disordered.

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