COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Assembly of supermolecular complexes from the tripodal ligand titmb: assembly of a large M_6L_8 cage from 14 components

Hong-Ke Liu*[a][b] and Xiaojun Tong[c]

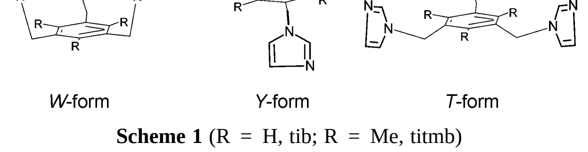
[a] *School of Chemistry, Zhongshan University, Guangzhou 510275, China. E-mail: hongke_liu@hotmail.com*
[b] *State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, China*
[c] *Department of Electrical and Computer Engineering, Rutgers University, Piscataway, NJ 08854, USA*

Received (in Columbia, MO, USA) 25th February 2002, Accepted 8th May 2002
First published as an Advance Article on the web 24th May 2002

The coordinatively saturated, nanometer-sized M_6L_8 complex $[Pd_6(titmb)_8]Cl_{12}·2H_2O$ (titmb = 1,3,5-bis(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene) was obtained by assembly of six Pd(II) ions with eight flexible titmb tripodal ligands; structural analysis shows that these eight titmb are in a disordered cube configuration and the six Pd atoms are in a disordered octahedral configuration; the inner cavity of the cage is estimated to have a volume of 1000 Å³, large enough to encapsulate eight Cl^- anions.

Many recent reports have focused on the assembly of cage-like complexes from metal ions and multidentate organic ligands,[1–4] for the reason that these complexes contain cavities which can encapsulate guest molecules or act as catalysts. Previous works show that tripodal ligands are among the most useful and several types of cage-like complexes have been synthesized and structurally characterized, for example, M_6L_4 cages have been obtained by reaction of the ligand 2,4,6- tris(4-pyridyl)-1,3,5-triazine (tpt)[3] with $Pd(en)(NO_3)_2$ or by reaction of 1,3,5-tris(pyrazol-1-ylmethyl)-2,4,6-triethylbenzene[4] with $PdCl_2$; an M_3L_2 cage-like complex has been assembled from 1,3,5-tris(4-pyridylmethyl)benzene[3] and $Pd(en)(NO_3)_2$. Most recently, Robson and coworkers[5] reported a large $M_{12}L_8$ type cage obtained by assembly of Cu(II) with a tris-bidentate ligand 2,4,6-triazophenyl-1,3,5-trihydroxybenzene (H_3tapp). These results imply that the assembly of the framework strongly depends on the nature of the ligands as well as the metal ions.

We have designed two tripodal ligands containing imidazolyl instead of the reported pyrazolyl and pyridyl groups: 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (titmb)[6–8] and 1,3,5-tris(imidazol-1-ylmethyl)benzene (tib).[9,10] These two ligands can adopt different conformations when they interact with metal ions: *cis,cis,cis*-conformation[6,8,9] (*W*-form), *cis-,trans,trans*-conformation (*Y*-form)[7] and *T*-form conformation[10] (Scheme 1). Our previous works have shown that the conformations of the tib and titmb are obviously controlled by the coordination number of the central metal ions, as well as the reaction conditions. When the coordination number (n) of metal ions are 4 or 2 and reaction is carried out in organic solvent, both titmb and tib adopt the *W*-form and prefer to form discrete cage-like complexes.[6,8,9] However, for coordination numbers $n > 4$ with water involved in the reaction, the two ligands appear in both *W*- and *Y*-form, or shows a novel *T*-form conformation (Scheme 1), and prefer to form extended structures.[7,10] Complexes with specific topologies such as two-dimensional network or cage-like structure can be expected to be obtained by reactions between the titmb or tib ligands of the *W*-form and metal ions of coordination number $n = 4$. In order to study the influence of metal ion stereochemical preference on the supramolecular construction and ligand conformation, a study was carried out with $Pd(CH_3CN)_2Cl_2$. Herein reported is the synthesis† and single crystal X-ray structure of a coordinatively saturated M_6L_8 nanometer-sized cage complex $[Pd_6(titmb)_8]Cl_{12}·2H_2O$ (**1**) assembled from titmb with $Pd(CH_3CN)_4Cl_2$. In this complex the titmb is indeed in *W*-form.



Scheme 1 (R = H, tib; R = Me, titmb)

Colorless crystals of solvated $[Pd_6(titmb)_8]Cl_{12}$ were obtained directly from aqueous acetonitrile containing titmb and $Pd(CH_3CN)_2Cl_2$ in 1 : 2 molar ratio, over a period of one month and the structure was characterized by crystallographic analysis.‡ Elemental analysis† of the complex is consistent with a formula of $[Pd_6(titmb)_8]Cl_{12}·2H_2O$ (**1**). The molecular structure of complex **1** is shown in Figs. 1 and 2. In complex **1**, the ligand titmb is in the *cis,cis,cis*-conformation and is unsymmetrically attached to three palladium atoms by the nitrogen atoms of the three imidazolyl arms. Each palladium atom is in turn coordinated by four imidazolyl groups from four ligands giving a distorted N_4 square-planar geometry (shown in Fig. 1(c)), with an average Pd–N bond length of 2.005 Å and N–Pd–N bond angles close to 90 or 180°.

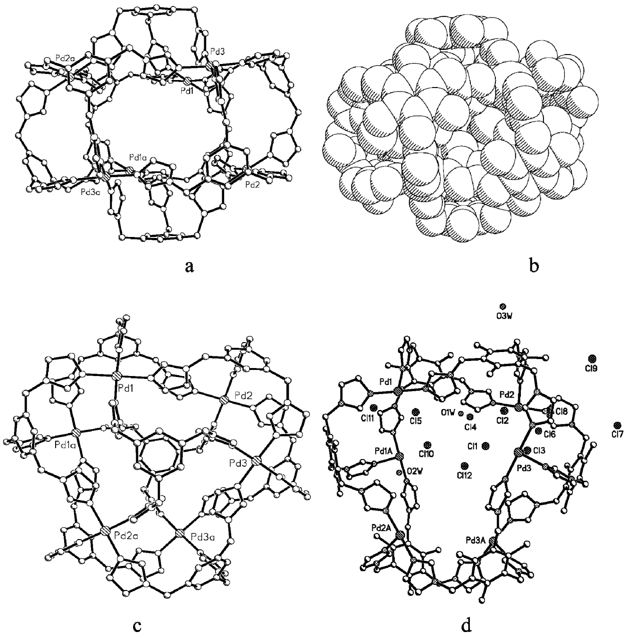
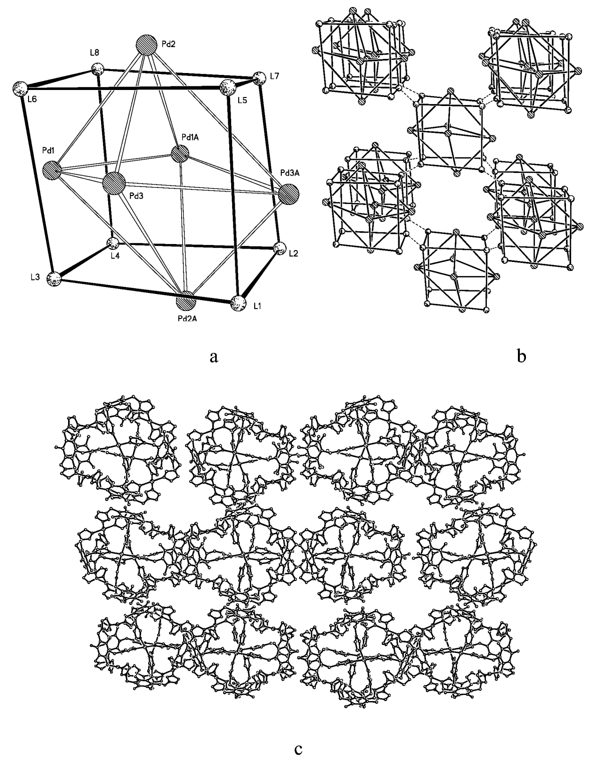


Fig. 1 Molecular structure of the M_6L_8 complex $[Pd_6(titmb)_8]Cl_{12}·2H_2O$ **1**. (a) Perspective view from the *y* axis; (b) space-filling representation and (c) top view. Methyl groups on the mesitylene rings, Cl^- anions, O and H atoms have been omitted for clarity. (d) Top view of the cage-like complex where the two top and bottom titmb ligands are omitted to show the encapsulated Cl^- anions. Selected atomic distances (Å) and bond angles (°): Pd1–N 1.991(4)–2.017(4); N–Pd1–N 88.14(16)–93.28(17)/176.51(16)–177.58(16); Pd2–N 1.982(3)–2.028(3), N–Pd2–N 89.34(15)–90.90(15)/177.22(14)–177.91(16); Pd3–N 1.974(4)–2.019(4), N–Pd3–N 88.12(17)–92.09(17)/176.40(15)–177.50(17); Pd1–Pd2 9.33, Pd2–Pd3 7.87, Pd1–Pd3 9.83 Å.

DOI: 10.1039/b201965e



a b

c

Fig. 2 (a) Schematic drawing of the $Pd_6(titmb)_8$ cage and (b) schematic drawing of the packing arrangement of the M_6L_8 cage complex. The solid spheres represent Pd atoms and the circles represent the centers of titmb phenyl rings, respectively. (c) The packing arrangement of this M_6L_8 cage complex along the *c* axis. The Cl^- anions, O and H atoms have been omitted for clarity.

The six Pd atoms and eight titmb are disposed around a central point and generate a coordinatively saturated M_6L_8 cage with low symmetry (only a 2-fold axis). Two of the titmb ligands which coordinate to Pd1, Pd2a, Pd3 and Pd1a, Pd2, Pd3a, individually, construct the top and the bottom of this large cage, with the mesityl groups almost parallel and facing each other at the two ends with a dihedral angle of only 14.83°. The distances from the cavity center to the centroids of these two mesitylene groups are exactly 7.4 Å. Each of the remaining six titmb also coordinate with three Pd atoms and construct the main body of the cage, distances from the cavity center to the centroids of those six mesitylene rings are all exactly 8.5 Å. Within the cage, the shortest and largest Pd–Pd distances are 7.76 and 13.18 Å, respectively. The dimension of the cage is 15 × 17 × 17 Å and the volume of the void inside the cage is estimated to be >1000 Å^3, sufficient in principle to accommodate many guest molecules of suitable size. The other interesting feature of this structure is its twelve flexible 24-membered ($Pd_2C_{14}N_8$) windows, constructed by the flexible methylene spacer groups. The average size of the windows is 9.5 × 9.8 Å, large enough to be channels for guest molecules. Analysis of the X-ray diffraction data indicates the order of twelve Cl^- anions and two H_2O molecules per cage, in which eight Cl^- anions (Cl1, Cl2, Cl3 Cl5, Cl8, Cl10, Cl11 and Cl12) are inside and the remaining four Cl^- anions (Cl4, Cl6, Cl7 and Cl9) and two water molecules are between the cages (Fig. 1(d)).

It is interesting to study the simplified topology structure and the packing arrangement of this M_6L_8 cage complex. This shows clearly (Fig. 2(a)) that the eight tripodal ligand titmb are in a disordered cube configuration, with centroid–centroid distances between the eight mesitylene groups of titmb within the cube configuration lying in the range 9.270–10.024 Å. Six Pd atoms are in a disordered octahedral configuration and each Pd atom is located out of the corresponding quadrangle planes formed by the centers of the four mesitylene groups of four titmb. The longest and shortest Pd–Pd distances within this octahedron are 7.706 and 9.930 Å. The packing arrangement of the M_6L_8 cages is shown in Fig. 2(b) and (c). Each of the eight mesitylene groups of an M_6L_8 cage are parallel to a nearby mesitylene group of eight adjacent M_6L_8 cages from eight directions, the distances between these mesitylene groups are in the range 3.743–5.051 Å, indicating that there are π–π interactions between the M_6L_8 cages. Thus, each M_6L_8 cage is linked to eight other cages *via* π–π interactions and a three-dimensional network is formed with the stacking sequence shown in Fig. 2(c), with all the solvent water molecules and unencapsulated Cl^- anions in the channels of the network.

In summary, a large, metal center coordinatively saturated, M_6L_8 cage-like complex $[Pd_6(titmb)_8]Cl_{12}\cdot 2H_2O$ (**1**) has been assembled by reaction of the flexible tripodal ligand titmb with $Pd(CH_3CN)_2Cl_2$. This is the first X-ray structure of a tripodal ligand-saturated cage. **1** also represents the first example of a large cage that can encapsulate up to 8 Cl^- anions. This work also represents the first example of a tripodal ligand affording both M_3L_2 and M_6L_8 cage complexes when reacted with different metal ions. Furthermore, this is the sixth example showing that the coordination number of the central metal ions can play an important role in the control of the conformations of the tripodal ligand tib and titmb. The result described here will be helpful to rationally design supermolecular complexes with special structures as well as properties. $[Pd_6(titmb)_8]Cl_{12}\cdot 2H_2O$ is soluble in DMSO and water and the study of the encapsulation reactions are still in progress.

The authors are grateful for the postdoctoral fund of Guangdong province for financial support of this work and for the help from Dr Su Chengyong and Dr Kang Beisheng at Zhongshan University.

Notes and references

† *Experimental*: a solution of titmb (72 mg, 0.2 mmol) in CH_3CN–H_2O (1 : 1) (10 ml) was added to an acetonitrile solution (10 ml) of $Pd(CH_3CN)_2Cl_2$ (26 mg, 0.1 mmol) at room temperature. The mixture was filtered after stirring for about 1 h and the filtrate was allowed to stand at ambient temperature for a month. Colorless crystals of complex **1** were collected in 41% yield (Found: C, 56.84; H, 5.42; N, 18.60. Calc. for $C_{168}H_{192}N_{48}Pd_6\cdot 2H_2O$ ($[Pd_6(titmb)_8]Cl_{12}\cdot 2H_2O$): C, 56.71; H, 5.55; N, 18.89%. ^{1}H NMR (D_2O, 308 K): δ 1.99 (s, 3H, CH_3), 5.20 (s, 2H, CH_2N), 6.71–7.40 (br, s, 3H, im H); im H refers to imidazole protons.

‡ *Crystal data* for **1**: $C_{168}H_{192}N_{48}Pd_6\cdot 2H_2O$, M_w = 3983.53, monoclinic, $C2/c$, a = 32.522(11), b = 36.623(12), c = 22.607(8) Å, β = 98.049°, U = 26661(16) Å^3, Z = 4, λ(Mo-Kα) = 0.560 mm^{-1}, T = 293(2) K, 61799 reflections collected, 21580 [$I > 2\sigma(I)$] oberserved; R_1 (wR_2) = 0.0976 (0.2708). CCDC reference number 159817. See http://www.rsc.org/suppdata/cc/b2/b201965e/ for crystallographic data in CIF or other electronic format.

1 D. J. Cram and J. M. Cram, *Container Molecules and their Guests*, Royal Society of Chemistry, Cambridge, UK, 1994; *Comprehensive Supramolecular Chemistry*, ed. J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vötle and J. M. Lehn, Pergamon, Oxford, 1996, vol. 9.
2 D. L. Caulder and K. N. Raymond, *Acc. Chem. Res.*, 1999, **32**, 975.
3 M. Fujita, D. Oguro, M. Miyazawa, H. Oka, K. Yamaguchi and K. Ogura, *Nature*, 1995, **378**, 469; M. Fujita, S. Nagao and K. Ogura, *J. Am. Chem. Soc.*, 1995, **117**, 1649.
4 C. M. Hartshorn and P. J. Steel, *Chem. Commun.*, 1997, 541.
5 B. F. Abrahams, S. J. Egan and R. Robson, *J. Am. Chem. Soc.*, 1999, **121**, 3535.
6 H-K. Liu, W-Y. Sun, W-X. Tang, T. Yamamoto and N. Ueyama, *Inorg. Chem.*, 1999, **38**((26)), 6313.
7 H-K. Liu, W-Y. Sun, H-L. Zhu, K-B. Yu and W-X. Tang, *Inorg. Chem. Acta*, 1999, **295**((2)), 129.
8 W.-Y. Sun, J. Fan, T. Okamura, J. Xie, K.-B. Yu and N. Ueyama, *Chem. Eur. J.*, 2001, **7**, 2557.
9 H-K. Liu, W-Y. Sun, D-J. Ma, K-B. Yu and W-X. Tang, *Chem. Commun.*, 2000, 591.
10 H-K. Liu, H.-Y. Tan, J.-W. Cai, Z.-Y. Zhou, A. S. C. Chan, S. Liao, W. Xiao, H.-X. Zhang, X.-L. Yu and S. Kang, *Chem. Commun.*, 2001, 1008.

Typeset and printed by Black Bear Press Limited, Cambridge, England