

# Assembly of a twin-cage complex containing a linear array of $\text{Pd}_3$ †

Hong-Ke Liu,<sup>ab</sup> Cheng-yong Su,<sup>a</sup> Cheng-Ming Qian,<sup>b</sup> Jun Liu,<sup>a</sup> Hai-Yan Tan<sup>a</sup> and Bei-Sheng Kang<sup>\*a</sup>

<sup>a</sup> School of Chemistry and Chemical Engineering, Zhongshan University, Guangzhou 510275, China

<sup>b</sup> State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, China

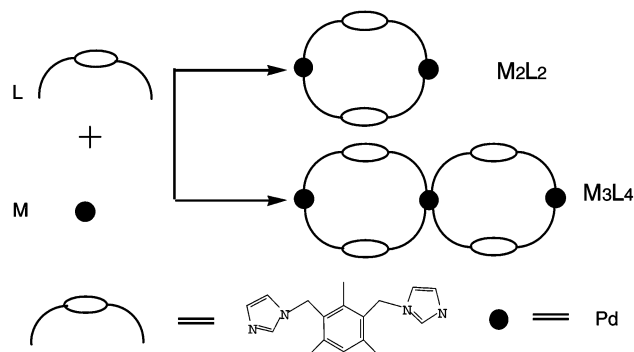
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The  $\text{M}_3\text{L}_4$  twin-cage complex  $[\text{Pd}_3(\text{bitmb})_4\text{Cl}_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O} \cdot \text{CH}_3\text{CN}$  [bitmb = 1,3-bis(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene] was obtained by assembly of three  $\text{Pd}(\text{II})$  ions with four molecules of the new flexible ditopic ligand bitmb; structural analysis showed that the complex contains two  $\text{M}_2\text{L}_2$  cages with a cavity size of ca. 200 Å<sup>3</sup>.

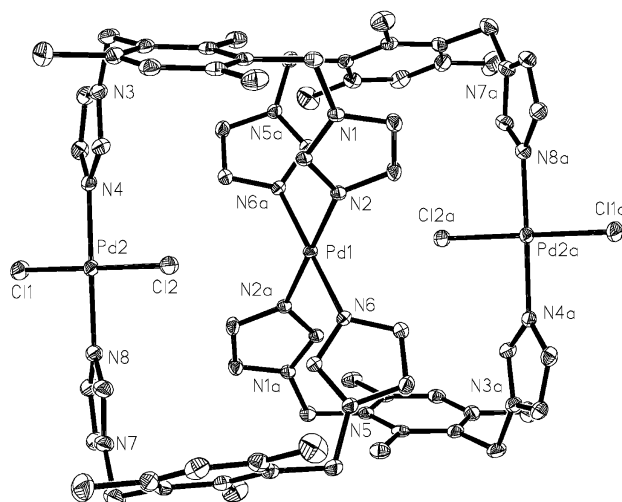
Assembly of complexes with inner cavities formed from metal ions and multidentate organic ligands has been a high profile topic in supramolecular chemistry in recent years.<sup>1–3</sup> The formation of such complexes has been successfully accomplished in two extreme areas: discrete cage-like<sup>4–6</sup> complexes with only one cavity and complexes with extended porous frameworks<sup>7–9</sup> containing innumerable cavities. However, discrete multicage or multicompartmental complexes are rare. It is important therefore that the formation of these species, which exhibit an abiological analogy to numerous biological processes mediated by collective interactions and recognition events between large molecules, be studied. Recently, Lehn<sup>10</sup> reported two multicompartmental nanoarchitectural complexes assembled by transition metal ions with two different multidentate ligands.

An  $\text{M}_2\text{L}_2$  cage can be assembled by combining two flexible bidentate ligands *L* of *cis* conformation with two transition metal ions *M*.<sup>11</sup> However, difficulty arises in how to combine two or more  $\text{M}_2\text{L}_2$  cages. In order to achieve this the following factors must be taken into consideration: (1) an adequately flexible bidentate ligand; (2) a transition metal ion with square-planar or octahedral geometry with a radius large enough to accommodate four 5- or 6-membered heterocycles; and (3) a counter-anion with moderate coordination capability are required. Scheme 1 depicts the assembly strategy of discrete multicage complexes. Herein we report the synthesis and characterization of the twin-cage complex  $[\text{Pd}_3(\text{bitmb})_4\text{Cl}_4]\text{Cl}_2 \cdot$



**Scheme 1** Assembly strategy of discrete multicage complexes.

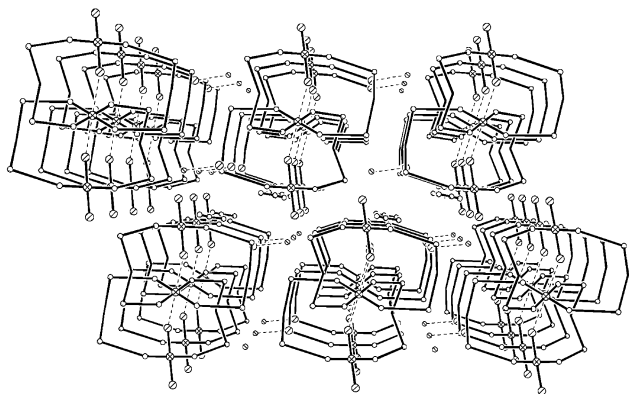
† Electronic supplementary information (ESI) available: structure of bitmb and view of a 1D chain of  $[\text{Pd}_3(\text{bitmb})_4\text{Cl}_4]\text{Cl}_2$  along the *x*-axis showing C–H...Cl hydrogen bonding. See <http://www.rsc.org/suppdata/dt/b1/b101691l/>



**Fig. 1** Molecular structure of the twin-cage complex  $[\text{Pd}_3(\text{bitmb})_4\text{Cl}_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O} \cdot \text{CH}_3\text{CN}$ . All the hydrogen atoms and solvate molecules and the uncoordinated  $\text{Cl}^-$  anions are omitted for clarity. Selected bond distances (Å) and angles (°): Pd1–N 2.014(3) ~2.021(3), N–Pd1–N 87.79(12) ~92.21(12)/180.00(11), Pd2–N 2.005(3) ~2.008(3), Pd2–Cl 2.2966(10) ~2.3005(11); N–Pd2–N 179.30(12), Cl–Pd2–Cl 177.64(5), N–Pd2–Cl 89.45(9) ~90.65(10), Pd1...Pd2 5.19.

$2\text{H}_2\text{O} \cdot \text{CH}_3\text{CN}$ , where bitmb is a new ditopic ligand 1,3-bis-(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene.

The ligand bitmb was prepared from 1,3-bis(bromomethyl)-2,4,6-trimethylbenzene and imidazole in a 1 : 2 molar ratio in DMSO under strong alkali (KOH) conditions.† This ligand is a derivation of 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene<sup>7</sup> but lacks an imidazol-1-ylmethyl group. Crystals of bitmb suitable for X-ray structural analysis§ (Fig. 1S) were obtained from a water solution containing ammonium hexafluorophosphate, which shows that the ligand in the solid state is in a *cis* conformation with two disordered hexafluorophosphate anions for each bitmb (omitted from Fig. 1S for clarity). Reaction of  $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$  with bitmb in an *M* : *L* ratio of 1 : 1 resulted in a pale yellow powder which was preliminarily identified as an  $\text{M}_2\text{L}_2$  cage complex with the formulation  $[\text{Pd}_2(\text{bitmb})_2\text{Cl}_4] \cdot 3.5\text{H}_2\text{O}$  (1)¶ which was confirmed by elemental analyses and FAB mass spectra. In order to obtain an  $\text{M}_3\text{L}_4$  twin-cage complex, an *M* : *L* ratio of 1 : 2 was used. Pale yellow sheet-like crystals of solvated  $[\text{Pd}_3(\text{bitmb})_4\text{Cl}_4]\text{Cl}_2$  suitable for X-ray structural analysis§ were obtained directly from the diffusion of diethyl ether into an acetonitrile–aqueous solution containing bitmb and  $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ . The formula  $[\text{Pd}_3(\text{bitmb})_4\text{Cl}_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O} \cdot \text{CH}_3\text{CN}$  (2) was confirmed by MALDI-TOF-MS measurements (*m/z*: 1619 [*M* – *Cl*]<sup>+</sup>) and elemental analyses.||



**Fig. 2** Stacking of the one-dimensional chains of the title complex in the  $yz$  plane with only skeleton atoms retained for clarity, the hydrogen bonds are indicated by dashed lines.

As shown in Fig. 1, the bitmb ligands in the structure of **2** are in a *cis* conformation and each is attached to two palladium atoms by a nitrogen atom of each imidazolyl groups. There are two different coordination environments for the three linearly arranged palladium ions: the central Pd(1) is coordinated by four N atoms from four bitmb ligands giving a distorted square-planar  $N_4$  geometry; while the terminal Pd(2) is coordinated by two N atoms from two bitmb and two Cl anions, obtaining a distorted square-planar  $N_2Cl_2$  geometry. The two square planes form a dihedral angle of  $26.7^\circ$ . The two *cis* bitmb ligands adopt a face-to-face orientation and are joined together by Pd(1) and Pd(2) to generate one  $M_2L_2$  cage, whilst another two bitmb are similarly oriented and generate another cage, and the two  $M_2L_2$  cages are linked together by Pd(1). Thus, the three linearly arranged metal atoms with a Pd(1)  $\cdots$  Pd(2) distance of 5.19 Å together with the two pairs of ligands generate a discrete  $M_3L_4$  twin-cage. In each  $M_2L_2$  cage, the two phenyl planes of bitmb are tilted with an angle of  $30^\circ$ , with a closest distance between the two ligands of 7.7 Å. The volume of the void space inside each cavity of an  $M_2L_2$  cage is estimated to be *ca.* 200 Å<sup>3</sup>, sufficient in principle to accommodate a guest molecule, like toluene.

Furthermore, an intriguing feature shown unambiguously by the crystallographic analysis of **2** is the packing arrangement of the twin-cages illustrated in Fig. 2 and Fig. 2S. As shown in Fig. 2S, each molecule encapsulates two phenyl rings of the bitmb ligands from neighboring molecules on two sides in opposite directions. Each encapsulated phenyl ring is parallel to one of the host phenyl rings with a center-to-center distance of 6.3 Å, but tilted from the other host phenyl ring, with an angle of  $30^\circ$  and a center-to-center distance of 5.8 Å. In addition, C–H  $\cdots$  Cl hydrogen bonds are formed between the methyl CH of one molecule and one of the coordinated chloride anions of a neighboring molecule with a C(25)  $\cdots$  Cl(2) distance of 3.39 Å (shown in Fig. 2S). Thus, the twin-cage molecules are linked by CH  $\cdots$  Cl to form one-dimensional chains along the  $x$ -axis and the stacking sequence is shown in Fig. 2, with all of the solvent molecules (water and acetonitrile) in the interspaces of the chains.

The results described here represent a new way to assemble twin-cage complexes from only one type of organic ligand, which largely simplifies current synthetic processes. It is also the first discrete  $M_3L_4$  twin-cage determined by X-ray crystallographic analyses to show a one-dimensional chain. The inner cavities of the two cages should be able to encapsulate one guest molecule each when the complex is dissolved in appropriate solvents. The encapsulation reactions and assembly of other discrete multicages (such as  $M_4L_6$  triplet-cage) are now being studied.

## Acknowledgements

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## Notes and references

‡ The ligand bitmb was prepared from 1,3-bis(bromomethyl)-2,4,6-trimethylbenzene and imidazole in a 1:2 molar ratio in dimethyl sulfoxide under strong alkaline (KOH) conditions in 70% yield. Found: C, 72.80; H, 7.16; N, 19.97. Calc. for  $C_{17}H_{20}N_4$ : C, 72.82; H, 7.19; N, 19.98%. <sup>1</sup>H NMR(CDCl<sub>3</sub>, ppm):  $\delta$  2.19(6H, s, CH<sub>3</sub>), 2.33(3H, s, CH<sub>3</sub>), 5.15(4H, s, CH<sub>2</sub>), 6.74(2H, s, <sup>4</sup>H<sub>im</sub>), 7.02(2H, s, <sup>5</sup>H<sub>im</sub>), 7.04(1H, s, H<sub>bz</sub>), 7.30(2H, s, <sup>2</sup>H<sub>im</sub>). H<sub>im</sub> refers to imidazole protons and H<sub>bz</sub> refers to phenyl ring protons.

§ Crystallography. The intensity data were collected on a Bruker CCD diffractometer with graphite-monochromated Mo-K $\alpha$  ( $\lambda = 0.71073$  Å) radiation at room temperature. All absorption corrections were performed using the SADABS program.<sup>12</sup> The structures were solved by direct methods and refined by full matrix least squares against  $F^2$  of all data using SHELXTL software.<sup>13</sup> For bitmb: formula  $C_{17}H_{20}N_4 \cdot 2H_2O$ ,  $M = 572.33$ , monoclinic,  $P2_1/c$ ,  $a = 8.556(3)$ ,  $b = 24.493(8)$ ,  $c = 11.792(4)$  Å,  $\beta = 110.170(5)^\circ$ ,  $U = 2319.5(14)$  Å<sup>3</sup>,  $Z = 4$ ,  $\mu(\text{Mo-K}\alpha) = 0.298 \text{ mm}^{-1}$ ,  $R_f(wR_2) = 0.0827(0.1856)$ . 8570 reflections collected, 2763 [ $I > 2\sigma(I)$ ] observed; for  $[Pd_3(\text{bitmb})_4Cl_4]Cl_2 \cdot 2H_2O \cdot CH_3CN$ ,  $C_{70}H_{87}N_{17}Cl_6O_2Pd_3$ , triclinic,  $P\bar{1}$ ,  $a = 10.9169(14)$ ,  $b = 13.9121(17)$ ,  $c = 14.0065(18)$  Å,  $\alpha = 69.913(2)^\circ$ ,  $\beta = 86.460(3)^\circ$ ,  $\gamma = 86.165(2)^\circ$ ,  $U = 1991.7(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $\mu(\text{Mo-K}\alpha) = 0.924 \text{ mm}^{-1}$ ,  $R_f(wR_2) = 0.0409(0.1008)$ . 13337 reflections collected, 6114 [ $I > 2\sigma(I)$ ] observed. CCDC reference numbers 154825 and 158770. See <http://www.rsc.org/suppdata/doi/10.1039/B101691I> for crystallographic data in CIF or other electronic format.

¶ A solution of bitmb (28 mg, 0.1 mmol) in acetonitrile–aqueous solution (10 ml) was added to an acetonitrile solution (10 ml) of  $Pd(CH_3CN)_2Cl_2$  (26 mg, 0.1 mmol) at room temperature with stirring. Standing the filtrate at room temperature results in a pale yellow powder, yield 10 mg (20%). Found: C, 41.51; H, 4.60; N, 11.25%. Calcd for  $[Pd_3(\text{bitmb})_4Cl_4] \cdot 3.5H_2O$ : C, 41.73; H, 4.84; N, 11.45%. <sup>1</sup>H NMR(CD<sub>3</sub>SOCD<sub>3</sub>, 293 K, ppm):  $\delta$  2.17(s, 6H, CH<sub>3</sub>), 2.50(3H, s, CH<sub>3</sub>), 5.31(4H, s, CH<sub>2</sub>), 6.90  $\approx$  7.69(7H, s, H<sub>im</sub> and H<sub>bz</sub>),  $M_{\text{calcd}} = 915.4$ , FAB-MS:  $m/z$ : 916 [ $M + H^+$ ].

|| A solution of bitmb (56 mg, 0.2 mmol) in acetonitrile–aqueous solution (15 ml) was added to an acetonitrile solution (10 ml) of  $Pd(CH_3CN)_2Cl_2$  (26 mg, 0.1 mmol) at room temperature with stirring. Diffusion of diethyl ether into the filtrate results in the formation of pale yellow crystals of the title complex, yield 15 mg (20%). Found: C, 48.28; H, 5.22; N, 13.20%. Calcd for  $[Pd_3(\text{bitmb})_4Cl_4]Cl_2 \cdot 2H_2O$ : C, 48.34; H, 5.01; N, 13.26%. <sup>1</sup>H NMR(CD<sub>3</sub>SOCD<sub>3</sub>, 315 K, ppm):  $\delta$  2.26(6H, s, CH<sub>3</sub>), 2.49(3H, s, CH<sub>3</sub>), 5.21(2H, s, CH<sub>2</sub>), 5.30(2H, s, CH<sub>2</sub>), 6.87–7.96(7H, H<sub>im</sub> and H<sub>bz</sub>),  $M_{\text{calcd}} = 1653.4$ , MALDI-TOF-MS(DMSO):  $m/z$ : 1619 [ $[Pd_3(\text{bitmb})_4Cl_4]Cl_2 - Cl]^+$ .

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