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Self-assembly of a novel macrotricyclic Pd(II) metallocage encapsulating a nitrate ion†

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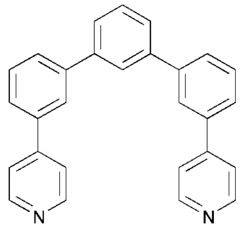
Complexation of the ligand 1 with $Pd(NO_3)_2$ leads to the self-assembly of a very stable M_2L_4 type macrotricyclic cage that encapsulates a nitrate ion inside its cavity.

Construction of discrete and well-defined molecular architectures using organic ligands and cleverly selected metal ions through the self-assembly route has received much attention during the last decade.[1] Desired species having predetermined structural and functional properties can be obtained by simply mixing the participating components under suitable conditions.[2] The self-assembled structures formed *via* a metal-driven self-assembly path can be classified logically under M_xL_y types (where M and L denote metal ions and ligands involved, respectively) with varying values of *x* and *y*. While previously reported cage structures are mostly formulated as M_3L_2,[3] M_6L_4,[4] or M_4L_6,[5] there is a scarcity in the series of M_2L_4 type cages[6] in the literature. Atwood and coworkers have reported an early example of a M_2L_4 cage[6a] where two octahedral copper(II) ions are bridged by four units of a bidentate ligand. While all the four equatorial positions of each copper ions are coordinated with the terminal pyridyl groups of the ligand strands, the axial positions are occupied by water molecules. Dinuclear copper(II) complexes of the M_2L_4 family having twisted structures and including chloride[6c] and perchlorate[6d] anions in between the metal centers are also reported. Another analogus structure is a dinuclear Pd(II) cage,[6b] with inclusion of hexafluorophosphate ion inside the cavity. However, in none of the cases the complexation reaction leading to the cage was directly monitored using NMR spectroscopy unlike our study in this work. Herein, we report the self-assembly of a novel macrotricyclic cage molecule from ligand **1** and $Pd(NO_3)_2$, the pivotal positions of the cage being occupied by Pd(II) ions. A nitrate ion is included inside the cavity in a cascade fashion bridging both the metal centers.



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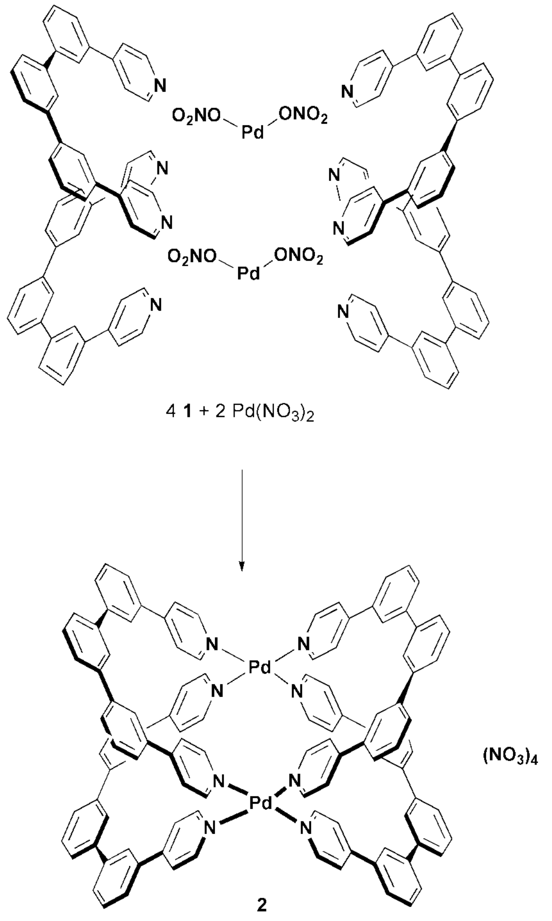
Ligand **1** was synthesized by Suzuki coupling of 1,3-bis(3-bromophenyl)benzene with 2-(4-pyridyl)-4,4,5,5-tetramethyl-1,3-dioxaborolane[7] using K_3PO_4 as base and $Pd(PPh_3)_4$ as catalyst.‡ The ligand **1** was mixed with $Pd(NO_3)_2$ at a ratio of 2 : 1 in DMSO and stirred at 90 °C for 1 day. Subsequently, addition of diethyl ether precipitated a pale yellow powder which was separated by filtration, washed with MeOH, and dried *in vacuo* to obtain the complex $[(Pd)_2(\mathbf{1})_4(NO_3)_4]$ **2**§ as a white solid in 74% yield (Scheme 1).



Scheme 1

Ligand **1** and complex **2** were characterised by ^1H and ^{13}C NMR. All the peaks were further completely assigned using H–H COSY and C–H COSY techniques. The signals for complex **2** as compared to ligand **1** in its proton NMR spectrum, particularly for py_α and py_β protons, were remarkably downfield shifted due to the complexation. A simple pattern of the spectrum suggests the formation of a discrete species (Fig. 1). Similarly ^{13}C NMR data also supports the assumed structure.¶ All the findings indicate that the four arms in complex **2** are equivalent and that four-fold symmetry axes pass through the metal centers in solution.

The same complexation reaction was also carried out in DMSO-d_6 and the solution was directly monitored by NMR spectroscopic means without isolating the complex. The spectrum obtained matched exactly that of the isolated complex. No peaks other than due to complex **2** were observed which establishes the quantitative self-assembly of **2**. When the metal

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† Electronic supplementary information (ESI) available: Crystallography section; Figs. S1–8: ^1H, ^{13}C, H–H and C–H COSY NMR spectra for **1** and **2**. See http://www.rsc.org/suppdata/cc/b1/b104853h/

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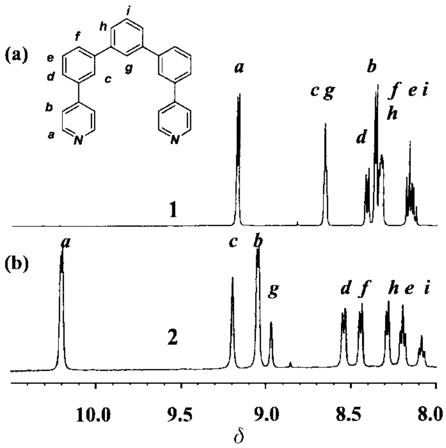

Fig. 1 ^{1}H NMR spectra of (a) ligand **1** and (b) macrotricyclic cage **2** (500 MHz, DMSO-d$_6$, 25 °C, TMS as an external standard).

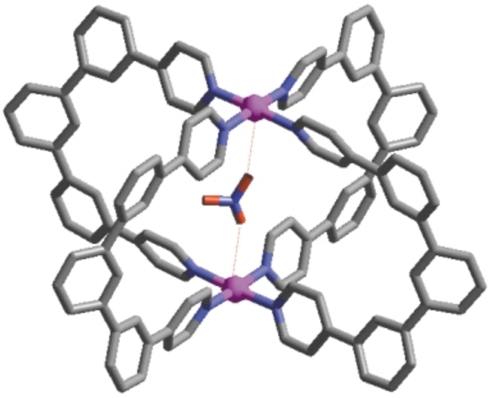

Fig. 2 Representation of $[(Pd)_2(\mathbf{1})_4(NO_3)]^{3+}$ in the crystal structure of **2** (Pd: ball mode and others: cylinder mode). The disorder of the nitrate anion is not shown. Key: palladium (magenta); nitrogen (blue); oxygen (red); carbon (gray).

salt was added in a lesser amount than the required stoichiometry for the complexation, all the signals of complex **2** were still observed, without any indication of any impurity, along with additional signals corresponding only to the uncomplexed free ligand. Also, by adding excess of the metal salt, no other new structures were suggestive from the NMR pattern. All these findings support the remarkable thermodynamic stability of **2**.

Finally, the structure of complex **2** was determined unambiguously from an X-ray diffraction study.‖ Needle-shaped crystals, suitable for X-ray diffraction analysis, were obtained in 2 days by layering diethyl ether over a solution of **2** in DMSO. A perspective view of the molecule is shown in Fig. 2. The crystal structure consists of the complexed cation $[(Pd)_2(\mathbf{1})_4(NO_3)]^{3+}$, three nitrate anions, nine DMSO and two diethyl ether molecules. Each Pd(II) has a square planar geometry with Pd–N bond distances in the range 2.024(7)–2.030(6) Å. The size of the 3-D cavity is *ca.* 11.1 × 10.2 × 8.4 Å which is defined by the arms of the rectangular array formed from four hydrogen centers, H_g (see Fig. 1 for labelling and Fig. 2 for comparison) and Pd–Pd separation. The cavity size after correcting for the van der Waals radius of the H centers is 8.7 × 7.8 × 6.0 Å . While three out of four nitrate ions stay outside of the cavity, one nitrate ion is encapsulated inside by ionic interactions, the Pd–O distance being 3.135(7) Å.

Analysis of crystal packing displayed the extension of intermolecular interactions in a linear manner, where three DMSO molecules lie in the intermolecular cavity formed in between two consecutive $[(Pd)_2(\mathbf{1})_4(NO_3)]^{3+}$ units (Fig. 3). The Pd–Pd axes of adjacent cages adopt a perpendicular geometry to each other making a hydrophobic pocket.

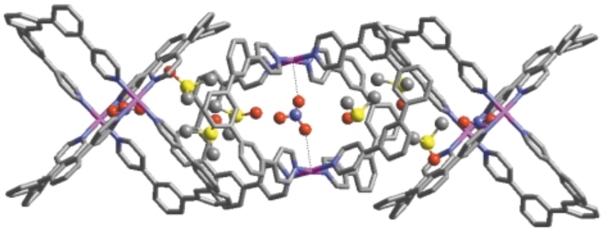

Fig. 3 Linear chain in the crystal structure of **2**. Three DMSO molecules are trapped in each of the intermolecular cavities. Key: palladium (magenta); nitrogen (blue); oxygen (red); sulfur (yellow); carbon (gray). The disorders of the nitrate anions and DMSO molecules are not shown.

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Notes and references

‡ Ligand **1**: a mixture of 1,3-bis(3-bromophenyl)benzene (0.3881 g, 1.0 mmol), 2-(4-pyridyl)-4,4,5,5-tetramethyl-1,3-dioxaborolane (0.5126 g, 2.5 mmol), K_3PO_4 (0.7429 g, 3.5 mmol), and $Pd(PPh_3)_4$ (0.1155 g, 0.1 mmol), was refluxed in 1,4-dioxane (25 mL) for 2 days at 100 °C under an argon atmosphere. After usual aqueous work-up the residue was chromatographed over silica gel to obtain a white soild, which was recrystallized from methanol affording **1** as white needles in 65% yield. δ_H (500 MHz, DMSO-d$_6$,TMS): 9.17 (d, 4H, a), 8.66(s, 2H, c), 8.65 (s, 1H, g), 8.41(d, 2H, d), 8.36 (d, 4H, b), 8.32–8.34 (m, 4H, f & h), 8.16 (t, 2H, e), 8.13 (t, 1H, i).δ_C (125 MHz, DMSO-d$_6$,TMS): 151.04 (a), 147.92 (C_q), 142.04(C_q), 141.51(C_q), 138.84(C_q), 130.70(e), 130.47(i), 128.86(d), 127.41(h), 126.97(f), 126.64(g), 126.45(c), 122.47(b); mp 192–193 °C, Anal. Calc. for $C_{28}H_{20}N_2{\cdot}0.3CH_3OH$: C, 86.12; H, 5.44; N, 7.09. Found: C, 86.17; H, 5.16, N, 7.07%.

§ Cage **2**: δ_H (500 MHz, DMSO-d$_6$,TMS): 10.18 (d, 16H, a), 9.20(s, 8H, c), 9.04 (d, 16H, b), 8.96(s, 4H, g), 8.53(d, 8H, d), 8.44 (d, 8H, f), 8.27 (d, 8H, h), 8.19 (t, 8H, e), 8.06 (t, 4H, i). δ_C (125 MHz, DMSO-d$_6$,TMS): 152.39 (a), 151.17 (C_q), 141.77(C_q), 140.58(C_q), 135.71(C_q), 131.12(e), 130.74(i), 130.25(f), 127.28(h), 127.19(c & d), 126.88(g), 125.61(b); mp decomp. at 289 °C), Anal. Calc. for $C_{112}H_{80}N_{12}O_{12}Pd_2{\cdot}6(CH_3)_2SO$: C, 60.36; H, 4.74; N, 6.81. Found: C, 60.12; H, 4.59, N, 6.80%.

¶ In the ^{13}C NMR spectrum of **2**, instead of 13 peaks only 12 peaks were observed. Here the signals of carbons c and d (see Fig. 1 for nomenclature) overlapped with each other as confirmed by the C–H COSY spectrum.

‖ *Crystal data* for **2**: $C_{112}H_{80}N_{12}O_{12}Pd_2{\cdot}9(CH_3)_2SO{\cdot}2(C_2H_5)_2O$, M = 2850.07, monoclinic, space group $C2/c$, a = 23.510(4), b = 22.229(3), c = 27.394(5) Å, β = 104.216(3)°, U = 13878(4) Å^3, T = 193 K, Z = 4, D_c = 1.364 g cm^{-3}, λ = 0.71073 Å, 36208 reflections measured, 12216 unique (R_{int} = 0.2039) which were used in all calcutations. $R1$ = 0.0766 and $wR2$ = 0.1676. Two of the nitrates and seven DMSO molecules were disordered.

CCDC reference number 164966. See http://www.rsc.org/suppdata/cc/b1/b104853h/ for crystallographic data in CIF or other electronic format.

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