A palladium metallacalix[4]arene capped with a gadolinium atom

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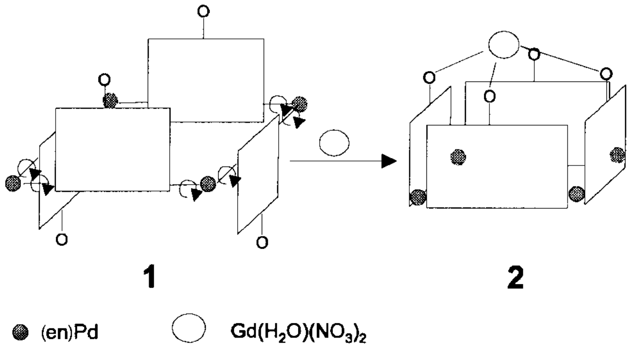
A molecular vase, analogous to a calix[4]arene, has been generated from (en)Pd^{II} and 4,6-dimethyl-2-hydroxypyrimidine, the X-ray crystallographic study showing that this compound is able to incorporate a gadolinium atom.

Calixarenes have been the subject of high interest owing to their wide range of applications.[1,2] Their cyclic frameworks associated with the presence of phenol oxygen atoms afford efficient complexing agents for metal ions,[3] while their hydrophobic cavities allow the inclusion of guest molecules. Formation of analogous inorganic macrocycles, metallacalixarenes, can be achieved by combining 120 and 90° bond angles provided respectively, by an appropriate ligand and a suitable metal entity.[4,5] Other angle combinations lead to molecular triangles,[6] squares,[7] and other structures of higher complexity.[8]

Reaction of $[(en)Pd(H_2O)_2]^{2+}$ with 4,6-dimethyl-2-hydroxypyrimidine (Hdmpymo) generates the cyclic species $[(en)Pd(dmpymo\text{-}N^1,N^3)]_4{}^{4+}$ **1**, (Scheme 1) by a self-assembly process. The presence of four exocyclic oxygen atoms of the pyrimidine moieties, suggested the possible coordination of additional metal atoms. Lanthanide metal ions were thought to be ideally suited in terms of both size and oxygen affinity. Addition of an excess of $Gd(NO_3)_3{\cdot}6H_2O$ to an aqueous solution of **1** affords $\{Gd(NO_3)_2(H_2O)[(en)Pd(dmpymo)]_4\}^{5+}$ **2** (Scheme 1),† which has been structurally characterised‡ and has been proved to be a metallacalix[4]arene of C_s symmetry (Fig. 1). The four Pd centres lie in a plane forming an almost perfect square with *ca.* 5.7 Å sides. The pyrimidine rings are not coplanar to the Pd_4 plane showing deviations of 35.2, 64.0 and 37.8°, respectively, for rings A, B and C, which results in the formation of a molecular vase. This is a consequence of Gd binding to the oxygen donor atoms of the dmpymo ligands which forces the four pyrimidine moieties to orient, from a high number of possibilities, in the same direction. The resulting conformation adopted by the metallacalixarene is that of a pinched cone. In classic organic calix[4]arenes stabilisation of the cone conformation, after binding of a single transition metal atom simultaneously to four phenol oxygens, is usual.[3] In metallacalix[4]arenes, however, the larger size of the oxo-surface, with O··O separations of *ca.* 4.4 Å, does not fit to transition metals, for which simultaneous binding to only two adjacent oxygen atoms has been observed.[9] The larger size of Gd^{3+} ideally suits the geometric requirements of the oxo-surface of **1** forming strong bonds to the four exocyclic dmpymo oxygens. The coordination sphere about Gd is completed by two bidentate nitrate anions placed over the calix lower rim and a water molecule completely encapsulated in the calix cavity. Calixarenes are well known for their ability to include guest molecules in their hydrophobic cavity.[1] Likewise, metallacalixarenes also possess a hydrophobic cavity which is also able to encapsulate organic residues.[9] In the present case, the opening of the cavity measured as the separation between C(5A)··C(5C) of 7.82(2) Å and C(5B)··C(5B#1) of 10.64(2) Å is big enough to permit inclusion of guest molecules. Additionally there is a water molecule coordinated to the Gd center which is completely included in the metallacalixarene cavity. This alters, the hydrophobic nature of the cavity[9] permitting the inclusion of an additional water molecule and a nitrate anion inside the cavity, which gives rise to strong H bonding interactions, namely O(1W)··O(5W) and O(1W)··O(91), with separations of 2.77(2) and 2.88(3) Å, respectively. This change in the hydrophobic nature of the cavity explains why it was not possible to find any host–guest chemistry of organic molecules for the $La[(en)Pt(uracilate)]_4(NO_3)_3$ species for which no X-ray structure was available.[9]

^1H NMR spectra of **1** are diagnostic of the N1, N3 bridging coordination mode of dmpymo, with retention of the original equivalence of its two methyl substituents. Replacement of the acidic protons at N1 and N3 in $H_2dmpymo^+$ by two metal entities is responsible for a significant downfield shift of the resonance of the aromatic proton H5 (−0.51 ppm) and upfield shift of the resonance of the methyl groups (δ +0.44 ppm) of dmpymo. The presence of only one set of dmpymo resonances in **1** is in agreement with its probable conformational flexibility.[5] We were also able to measure the ^1H NMR spectrum of **2** even thought it is paramagnetic. The spectrum is more complex than that of **1** with now two sets of signals for the



Scheme 1 Metallacalix[4]arene **1** presents conformational flexibility as a consequence of free rotation about the Pd–dmpymo bonds. In **2** Gd coordination to the oxo-surface of the metallacalix[4]arene is responsible for its fixed cone conformation.

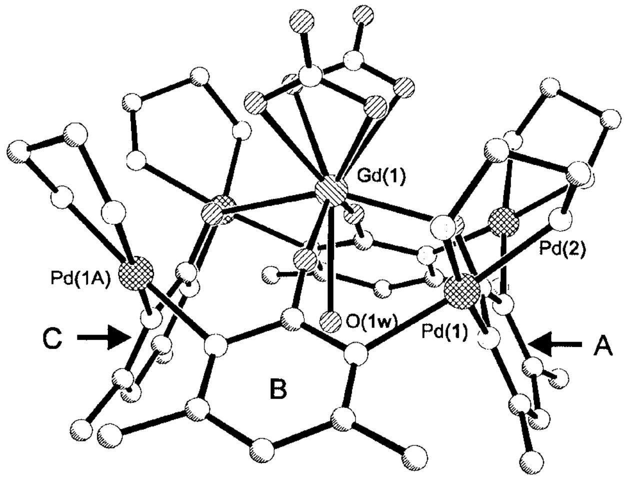


Fig. 1 Perspective view of the cation $\{Gd(NO_3)_2(H_2O)\ [(en)Pd(dmpymo)]_4\}^{5+}$ in the crystal structure of **2**. Pyrimidine rings A, B and C are labelled. Selected band lengths (Å): Gd(1)–O(2A) 2.309(8), Gd(1)–O(2C) 2.306(8), Gd(1)–O(2B) 2.323(6), Gd(1)–O(1W) 2.49(1), Gd(1)–O(41) 2.504(6), Gd(1)–O(31) 2.535(6), Pd(1)–N(1C) 2.071(7), Pd(1)–N(3B) 2.087(7), Pd(2)–N(3A) 2.072(7), Pd(2)–N(1B) 2.082(7).

dmpymo resonances of H5 (δ 6.31, 6.58) and methyl protons (δ 2.86, 3.04). We believe this can be attributed to the increased rigidity introduced to the metallacalixarene after Gd^{3+} coordination to **1**. Addition of La^{3+} has, however, no effect on the resonances of **1**. It is thought that the more polarising nature of Gd^{3+} with respect to La^{3+} leads to stronger bonds to the oxygen donor atoms of **1**.

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Notes and references

† $[(en)Pd(dmpymo)]_4(NO_3)_4$ **1** was obtained as follows: $(en)PdCl_2$ (3 mmol) was suspended in water (30 mL), $AgNO_3$ (6 mmol) added and the mixture stirred for 2 h at 60 °C. The mixture was cooled and AgCl removed by filtration. Hdmpymo (3 mmol) was added to the filtrate, at this point the pH was adjusted to 5.0 by means of 1 M NaOH, and the resulting pale yellow solution heated to 60 °C for 5 h. Subsequent concentration of the solution to 15 mL by rotary evaporation gives **1** in 32% yield, after 7 days at room temperature. Satisfactory elemental analysis for $C_{32}H_{68}N_{20}O_{20}Pd_4$: Anal. Calc. for **1**: C, 25.99; H, 4.64; N, 18.94. Found: C, 25.76; H, 4.99; N, 18.98%. δ_H(300 MHz, D_2O): 2.77 (CH_2, s, 4H), 3.02 (CH_3, s, 3H), 6.26 (H5, s, 1H). $\{Gd(NO_3)_2(H_2O)[(en)Pd(dmpymo)]_4\}(NO_3)_5\cdot 8H_2O$ **2** was obtained after adding an excess of $Gd(NO_3)_3\cdot 6H_2O$ (1 mmol) to an aqueous solution of **1** (0.125 mmol in 10 mL of H_2O). The resulting solution (pH 2.6) affords, after one week, yellow crystals of **2** in low yield (9%). Satisfactory elemental analysis for $C_{32}H_{76}N_{23}O_{33}Pd_4Gd$: Anal. Calc. for **2**: C, 20.29; H, 4.04; N, 17.01. Found: C, 20.13; H, = 3.98; N, 16.90. δ_H(400 MHz, D_2O): 2.77 (CH_2, s, 4H), 2.86, 3.04 (CH_3, s, 3H), 6.31, 6.58 (H5, s, 1H).

‡ *Crystal data* for **2**: M = 1876.0, orthorhombic, space group *Pnma*, a = 26.883(1), b = 13.2671(7), c = 17.961(1) Å, U = 6405.8(5) $Å^3$, Z = 4, D_c = 1.964 g cm^{-3}, μ = 2.228 mm^{-1}, λ(Mo-Kα) = 0.71069 Å, F(000) = 3764, T = 293(2) K. Stoe STADI4 diffractometer, crystal size 0.550 × 0.397 × 0.280 mm, 8075 reflections measured, 7668 unique, reflections observed 4269 $F_o^2 > 4\sigma(F_o^2)$, R_1 = 0.0590, wR_2 = 0.1489 (observed data), S = 1.029. The structure was solved by the Patterson method and refined using least-square methods.[10] The disorder found in one of the nitrate anions was modelled considering two positions with half occupancy. All non-hydrogen atoms were refined anisotropically with the exception of some of the nitrate anions and water molecules. CCDC 182/1515. See http://www.rsc.org/suppdata/cc/a9/a909150e/ for crystallographic files in .cif format.

1 C. D. Gutsche, *Calixarenes*, Royal Society of Chemistry, Cambridge, 1989; V. Böhmer, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 713; A. Ikeda and S. Shinkai, *Chem. Rev.*, 1997, **97**, 1713.

2 See, for example: G. G. Talanova, H.-S. Hwang, V. S. Talanov and R. A. Bartsch, *Chem. Commun.*, 1998, 1329; B. Xu and T. M. Swager, *J. Am. Chem. Soc.*, 1993, **115**, 1159.

3 C. Wieser, C. B. Dieleman and D. Matt, *Coord. Chem. Rev.*, 1997, **165**, 93; V. C. Gibson, C. Redshaw, W. Clegg and M. R. J. Elsegood, *Chem. Commun.*, 1998, 1969; L. Charbonnière, C. Balsiger, K. J. Schenk and J.-C. G. Bünzli, *J. Chem. Soc., Dalton Trans.*, 1998, 505; L. Giannini, E. Solari, A. Zanottigerosa, C. Floriani, A. Chiesivilla and C. Rizolli, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 753.

4 H. Rauter, E. C. Hillgeris, A. Erxleben and B. Lippert, *J. Am. Chem. Soc.*, 1994, **116**, 616; H. Rauter, I. Mutikainen, M. Blomberg, C. J. L. Lock, P. Amo-Ochoa, E. Freisinger, L. Randaccio, E. Zangrando, E. Chiarparin and B. Lippert, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1296.

5 J. A. R. Navarro, E. Freisinger and B. Lippert, *Inorg. Chem.*, submitted.

6 R.-D. Schnebeck, L. Randaccio, E. Zangrando and B. Lippert, *Angew. Chem., Int. Ed.*, 1998, **37**, 128; R.-D. Schnebeck, E. Freisinger and B. Lippert, *Chem. Commun.*, 1999, 675.

7 M. S. Lüth, E. Freisinger, F. Glahé and B. Lippert, *Inorg. Chem.*, 1998, **37**, 5044; M. Fujita, J. Yazaki and K. Ogura, *J. Am. Chem. Soc.*, 1990, **112**, 5645.

8 A. J. Stemmler, J. W. Kampf, M. L. Kirk, B. H. Atasi and V. L. Pecoraro, *Inorg. Chem.*, 1999, **38**, 2807; D. W. Johnson, J. Xu, R. W. Saalfrank and K. N. Raymond, *Angew. Chem., Int. Ed.*, 1999, **38**, 3058.

9 J. A. R. Navarro, M. Janik, E. Freisinger and B. Lippert, *Inorg. Chem.*, 1999, **38**, 426.

10 G. M. Sheldrick, SHELX-97, Program for structure solution and refinement, University of Göttingen, Germany, 1997.

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