

On the structure of transition-metal-linked molecular squares

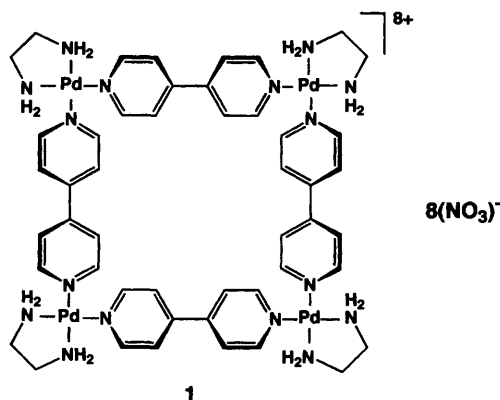
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The structure of a molecular square assembling from [Pd(en)(NO₃)₂] **3** and 4,4'-bipyridine is confirmed by X-ray crystallography, whereas squares assembling from **3** and larger ligands, py-X-py (py = 4-pyridyl, X = CH=CH, C≡C, *p*-C₆H₄) are shown to exist in equilibrium with molecular triangles.

Since we first reported the self-assembly of square supramolecule **1** in 1990,¹ there have appeared many molecular squares^{2,3} in which transition metals, hypervalent iodine, or organic frameworks provide the 90° angle at the four edges of the square. It seems that these reports have made an impression that the combination of a right-angular component and a linear one always gives rise to the self-assembly of molecular squares. Such an understanding is, however, not fully consistent with our earlier results accumulated before 1990: although we observed the quantitative self-assembly of **1**, square molecules existed in equilibrium with another structure when bipyridine or ethylenediamine ligands were replaced with larger ligands. Such observations as well as considerable current interest in the square structure⁴ prompted us to communicate our earlier⁵ and recent results on the structure of molecular squares, warning that a reliable method is required for studying their structures. Here, the following aspects are described. (i) Both the solid and solution structures of **1** were fully characterized. (ii) A molecular square exists in equilibrium with another discrete structure most probably assigned as a molecular triangle.



An X-ray diffraction study of **1** was carried out with a single crystal of a 1:1 clathrate complex of **1** and naphthalene obtained from a methanol-water (19:1) solution of **1** (6.3 mmol dm⁻³) in the presence of naphthalene (130 mmol dm⁻¹). The diffraction analysis showed the existence of an almost perfect square structure of **1** with facial conformation of pyridine nuclei (Fig. 1).[‡] The unit cell involves three crystallographically independent centrosymmetric molecules of **1**, which have similar conformations. Unfortunately, the naphthalene molecules, nitrate ions, and waters of crystallization were highly disordered and some molecules could not be located. The formula of the clathrate was shown to be **1**·C₁₀H₈·*n*H₂O (*n* = ca. 14) by elemental analysis [Anal: Calc.

for **1**·C₁₀H₈·14H₂O: C, 32.14; H, 4.65; N, 15.51. Found: C, 31.75; H, 4.43; N, 15.83%]. Single crystals of the clathrate of **1** were also obtained with such guests as *p*-dimethoxybenzene, *p*-dibromobenzene and ferrocene; **1** itself crystallized even in the absence of a guest. However, these crystals were too unstable to be subjected to crystallographic analysis. The solution structure of **1** is convincing because, in addition to satisfactory NMR data, ESIMS supported the molecular mass of **1**: *m/z* 830 [M - 2NO₃]²⁺, 533 [M - 3NO₃]³⁺, 384 [M - 4NO₃]⁴⁺.

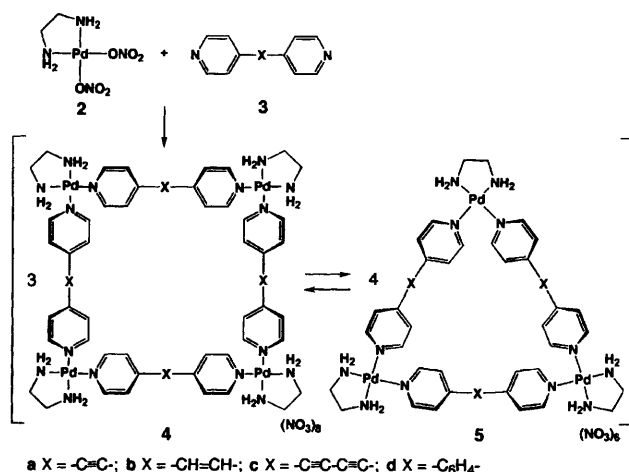
Besides a molecular square, another component with a highly symmetric structure was formed as a minor product when 4,4'-bpy was replaced by a larger bridging ligand **3**. Thus, two components were assembled from [Pd(en)(NO₃)₂] **2** and bis(4-pyridyl)acetylene **3a**. Both products should have macrocyclic structures because all the pyridine nuclei in each structure are completely equivalent on the basis of NMR (PyH α : δ 8.69, PyH β : δ 7.64, for the major component; PyH α : δ 8.67, PyH β : δ 7.59, for the minor component) and satisfactory elemental analysis data were obtained. The major product is assigned as the most stable square **4a** by analogy with the structure of **1**. We assigned the minor product as the second most stable compound; this should be the molecular triangle **5a** (Scheme 1). These assignments were strongly supported by concentration effects on the equilibrium ratio: at higher concentration, the ratio shifted toward the triangle producing three molecules of **4a** from four molecules of **5a** (Table 1). Ligands **3b** and **3c** also afforded equilibrium mixtures of two components assigned as squares and triangles. From **3d**,⁶ the formation of oligomeric products became significant at high concentrations in addition to the formation of **4d** and **5d**. The equilibration stems from a thermodynamic balance: strainless square **4** is more stable in terms of enthalpy, whereas entropy effects favour triangle **5** since **5** assembles from fewer components than **4**.^{§¶}

It was found that even 4,4'-bpy afforded a mixture of two components assignable as square **6** and triangle **7** when the ethylenediamine protective group was replaced by 2,2'-bpy (Scheme 2). The equilibrium ratios **6**:**7** are 66:34, 58:42,



Fig. 1 A CPK presentation of the crystal structure of **1**. Only one of the three independent centrosymmetric molecules of **1** is shown.

47:53, 39:61 and 28:72 at 20, 10, 5, 3 and 1 mmol dm⁻³, respectively. Probably, steric repulsion between 2,2'-bpy and 4,4'-bpy pushes the equilibrium toward **7** to some extent. The possibility of the formation of triangles in solution has never been discussed in previous papers.^{2,3} Although our evidence for molecular triangles is not watertight, the present work suggests at least the formation of a variety of polynuclear species in solutions which had previously been thought to contain only self-assembled molecular squares.

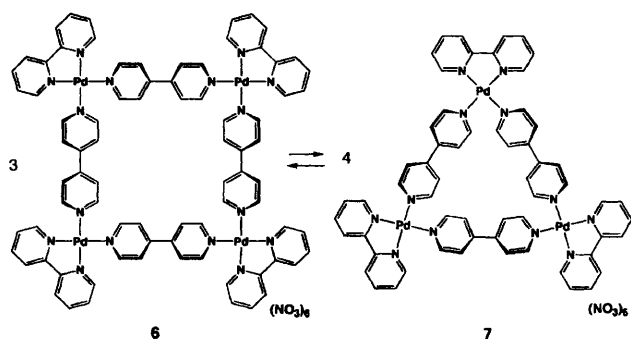


Scheme 1 An equilibration between self-assembled molecular square **4** and triangle **5**

Table 1 Equilibrium ratios between **4** and **5** (D₂O, 25 °C)

[Pd] _{net} (mmoldm ⁻³)	4a : 5a	4b : 5b	4c : 5c	4d : 5d
80	90 : 10	88 : 12	— ^a	— ^a
40	86 : 14	85 : 15	81 : 19	— ^b
20	83 : 17	81 : 19	79 : 21	92 : 8 ^c
8	77 : 23	77 : 23	64 : 36	88 : 12 ^d
2	59 : 41	— ^a	50 : 50	70 : 30 ^e

^a Not determined. ^b Oligomers were mainly formed (>95%). ^c Oligomers: (**4d** + **5d**) = 54:46. ^d Oligomers: (**4d** + **5d**) = 12:88. ^e Oligomers were not detected.



Scheme 2

Footnotes

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‡ *Crystallography*: a laser-stimulated fluorescence image plate was used as a two-dimensional area detector for the diffraction study of the clathrate complex: formula, [C₁₀H₈·14H₂O]_{1.5} = C₈₇H₁₅₀N₃₆O₅₇Pd₆; *M* = 3250.88; triclinic, space group *P* $\bar{1}$ (no. 2); *a* = 19.105(7), *b* = 22.164(5), *c* = 19.161(9) Å, α = 109.53(3), β = 97.19(4), γ = 107.38(3)°, *U* = 7065(5) Å³; *Z* = 2; *D*_c = 1.53 g cm⁻³, *F*(000) = 3000, μ (Mo-K α) = 8.29 cm⁻¹; λ (Mo-K α) = 0.7107 Å, *T* = -100 °C; 12666 reflections measured, 7708 observed [*F* > 4.50 σ (*F*)]; number of parameters 1031; *R* = 0.189, *R*_w = 0.226. The low quality is due to a high degree of disorder of the naphthalene molecules, nitrate ion, and water of crystallization which were not located. 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 182/82.

§ Temperature effects are also consistent with our assignment: the equilibrium ratio shifted toward the entropically more favourable molecular triangle upon heating.

¶ *Self-assembly of 4 and 5*. A typical procedure: An aqueous solution (2 mmol dm⁻³) of **2** (0.10 mmol) was added to a methanol solution (0.5 ml) of **3a** (0.10 mmol) at ambient temperature. After 5 min, addition of an aqueous solution (2 ml) of NaClO₄ (0.40 mmol) precipitated a colourless powder, which was filtered off and washed with a small amount of ethanol to give a mixture of **4a** and **5a** (ClO₄ salt, 70%, mp 195 °C decomp.). Anal: Calc. for [C₁₄H₁₆Cl₂N₄O₈Pd·H₂O]_{*n*} (*n* = 4 **4a**, 3 **5a**): C, 29.83; H, 3.22; N, 9.94. Found: C, 29.81; H, 3.07; N, 10.00%. ¹H NMR (500 MHz, D₂O, 25 °C, SiMe₄-CDCl₃ in a capillary): signals used for the determination of the ratio **4a** : **5a**: δ 7.64 for **4a**, δ 7.59 (d, *J* = 6.6 Hz, PyH β) for **5a**.

5b and **6b**: 82% (86% as ClO₄ salt); mp 245 °C decomp. Anal: Calc. for [C₁₄H₁₈Cl₂N₆O₆Pd·1.75H₂O]_{*n*} (*n* = 4 **4b**, 3 **5b**): C, 33.35; H, 4.30; N, 16.67. Found: C, 33.25; H, 4.30; N, 16.56%. Signals in ¹H NMR used for the determination of the ratio **4b** : **5b**: δ 7.43 for **4b**, δ 7.29 (s, CH) for **5b**.

4c and **5c**: The NMR yield of **4c** + **5c** was quantitative (not isolated). Signals used for the determination of the ratio **4c** : **5c**: δ 7.64 for **4c**, δ 7.59 (d, *J* = 6.6 Hz, PyH β) for **5c**.

4d and **5d**: Signals in ¹H NMR used for the determination of the ratio **4d** : **5d**: δ 7.91 for **4b**, 7.81 (s, CH) for **5d**.

Self-assembly of 6 and 7: 92%, mp >300 °C decomp. Signals used for the determination of the ratio **6** : **7**: δ 9.10 for **6**, 8.94 (d, *J* = 6.6 Hz, PyH α) for **7**.

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