DOI: 10.1002/ejic.200701189

Steric Effects in the Self-Assembly of Palladium Complexes with Chelating Diamine Ligands

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Keywords: Steric effects / Self-assembly / Supramolecular chemistry / Trimer/tetramer equilibrium / DOSY / X-ray diffraction

The influence of the steric properties of chelating diamines on the self-assembly of $[Pd(N^{\cap}N)](NO_3)_2$ complexes with 4,4′-bpy as bridging ligand has been studied by ^1H NMR spectroscopy and X-ray diffraction ($N^{\cap}N$ = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, *N*,*N*,*N*′,*N*′-tetraethylethylenediamine, 1,3-diaminopropane, *N*,*N*′-dimethylpiperazine, homopiperazine and ethylenediamine). Based on crystallographic data, the steric bulk of the chelating amines in the $[Pd(N^{\cap}N)]^{2+}$ cations has been characterised in two different ways. A temperature- and concentration-sensitive trimer/tetramer equilibrium was observed by NMR spectroscopy with every diamine, in which the trimeric species dominated when the chelating amine was the bulky tetraethylethylenediamine. Although the formation of tetramers was preferred with diamines of decreasing steric demands, trimeric aggregates could be observed even with the least congested homopiperazine and ethylenediamine complexes. The distribution of the tectons between the two constituents follows the trend predicted by the steric features of the coordinated diamine ligands. Diffusion NMR spectroscopy has proved to be an efficient tool in the identification of self-assembled species. The trimer/tetramer equilibrium established with tetramethylethylenediamine as chelating ligand has been observed in solution by using wide-angle X-ray diffraction.

Introduction

Spontaneous organisation of molecular building blocks into predesigned supramolecular coordination compounds has been extensively studied for more than 15 years.[1] At first, the intention to mimic various geometrical shapes and forms by self-assembled species was the major driving force of the worldwide research activity. In recent years, the interest in multimetallic supramolecular complexes has been strengthened by the recognition that these nanostructures, for example, may form host/guest complexes,[2] can provide a unique environment in their internal cavities for catalytic reactions[3] and may find applications in various fields of nanotechnology.[4]

In order to construct self-assembled aggregates mimicking various geometrical forms, researchers have mainly relied on the high directionality encoded into the positions of the coordination sites.[5] It has also been demonstrated that parameters such as tecton concentration, temperature, the chemical nature of the solvent and the anion, and incorporation of guest molecules may also affect the composition of the reaction mixture. To the best of our knowledge, no systematic study has been carried out, however, to explore the effects of the steric properties of the chelating ligands. Keeping the varied fields of chemistry in mind where the influence of the ligand bulk has been documented,[6] the relative disinterest in the steric features of the metal-anchored ligands is surprising. Sporadic literature data do indicate that steric interactions may play a crucial role in determining the nuclearity of the self-assembled products. For example, the palladium(2+) ion ligating bis(diphenylphosphanyl)ethane forms the trimeric $[Pd(dppe)(\mu\text{-}CN)]_3^{3+}$ cation[7] in contrast to the quadratic arrangement of the $[Pd(C_6F_5)(PEt_3)(\mu\text{-}CN)]_4$ species bearing the sterically less demanding C_6F_5 moiety at one of the coordination sites.[8] The influence of steric congestion on the shape of the molecules may also be suspected if we compare the supramolecular compounds assembled in the interaction of $[Pt(dppp)]^{2+}$ and $[Pd(en)]^{2+}$ corner elements with 4,4′-bpy or pyrazine ligands. While the relatively long 4,4′-bpy yields molecular squares with both acceptor tectons,[9] the shorter pyrazine results in tetrameric $[Pd(en)(pyr)]_4^{8+}$ adducts if the chelating agent is ethylenediamine[10] but forms trimeric $[Pd(PMe_3)_2(pyr)]_3^{6+}$ complexes if the *cis* coordination sites are occupied by bulky trimethylphosphane ligands.[11]

It seems plausible to attribute the emergence of the trimeric or tetrameric species to the steric properties of the respective corner elements. However, the major drawback of comparing observations from various literature sources

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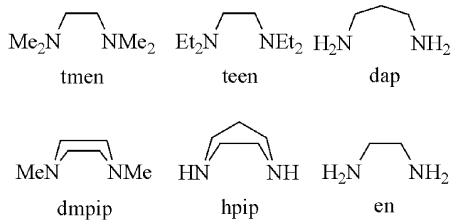
is that it is not systematic, because simultaneous changes of more than one essential parameter, like the chemical nature of the metal centre, the electronic properties of the ligands, and the coordinating ability of the solvent and the anion, hamper unambiguous conclusions.

The aim of the present work is to study the potential extent of the steric interactions by monitoring the composition of reaction mixtures formed in the reaction of 4,4′-bpy as bridging ligand with a series of $[Pd(N^{\cap}N)](NO_3)_2$ complexes while keeping all parameters (temperature, concentration, solvent, etc.) constant. Diffusion-ordered NMR spectroscopy (DOSY)[12] has proved to be a reliable method for ready identification of the molecular squares and triangles based on the measurement of their longitudinal diffusion constants. The ability of wide-angle X-ray diffraction to identify a triangle/square equilibrium in solution has also been documented.

Results and Discussion

Steric Properties of Selected Diamines

In order to shed light on the manifestation of steric effects in a self-assembly process, we have chosen the $[Pd(N^{\cap}N)]^{2+}$/4,4′-bpy system for several reasons ($N^{\cap}N$ denotes a chelating aliphatic diamine). First, aliphatic diamines seemed to be highly suitable chemicals for a systematic investigation of steric effects because changing the backbone between the donor atoms or replacing the NH hydrogen atoms for bulkier groups offer an easy way to adjust the steric properties according to our purposes. Second, the pioneering work of Fujita et al.[1a] has shown that the self-assembled molecular square can be observed as a single product in the reaction of $[Pd(en)]^{2+}$ with 4,4′-bpy, indicating that a negligible steric hindrance can be expected with this diamine. It was of primary importance for us to vary the bulkiness of the chelating ligand without changing the electronic properties and, therefore, all the diamines studied here are of purely σ-donor character. An overview of complexes incorporating chelating diamines has shown that a simple series of easily accessible ligands comprising tetramethylethylenediamine (tmen), tetraethylethylenediamine (teen), 1,3-diaminopropane (dap), *N*,*N*′-dimethylpiperazine (dmpip), homopiperazine (hpip), and ethylenediamine (en), may be suitable for the synthesis of corner elements possessing sufficiently different steric properties (Scheme 1).



Scheme 1.

As a measure of bulkiness, the cone angle θ,[13] the solid angle Ω[14] and the ligand repulsive energies E_r[15] are most commonly employed. Recently, based on solid angles, a new measure, the *G* parameter, has been suggested to characterise the accessibility of the metal centre by an incoming ligand.[16] The overwhelming majority of the studies on steric properties have been devoted to phosphanes, although ligands with N, C, As or S donor atoms as well as olefins have also attracted considerable interest.[6a–6c,17] We are not aware, unfortunately, of investigations related to the steric characterisation of chelating aliphatic diamines. We hoped, however, that crystallographic data could provide us with a solid basis to assess the steric bulk of coordinated diamines. As a source of data, the Cambridge Crystallographic Data Base (CCDB)[18] was used. First, a group of complexes incorporating the diamines listed above was selected.[19] In order to estimate the steric requirement of the chelating ligands, X-ray diffraction data were utilised in two different ways. On one hand, distances and angles that may be relevant to the extent of the coordinated diamines have been collected. As a second approach, we employed the atomic coordinates of the same complexes[19] as input data for the program Solid-G that has been developed recently by Guzei and co-workers to calculate steric properties of organometallic compounds.

Direct Estimation of Bulkiness from Crystallographic Data

As we are currently interested in the chemistry of palladium complexes with the potential extension of our studies to platinum, we have restricted our search in the CCDB to the diamine complexes of these two metals. The averages of the bond lengths and angles allowing an assessment of the steric requirements of the coordinated diamine ligands are presented in Table 1.

Although the slight elongation of the M–N bond within the en, tmen, teen series may be reasonably attributed to

Table 1. Selected distances and angles related to the bulkiness of coordinated diamines.

	en	tmen	teen	hpip	dmpip[20]	dap
d(M–N)/Å	2.024(0.027)	2.058(0.018)	2.082(0.054)	2.026(0.019)	2.062(0.003)	2.045(0.014)
ϕ(N–M–N)/°	83.67(0.85)	85.73(0.84)	84.37	77.32(1.21)	72.56(0.49)	91.56(1.66)
d(N···N)/Å	2.700(0.032)	2.798(0.023)	2.796	2.532(0.054)	2.440(0.011)	2.929(0.047)
ϕ(H···M···H)/°	114.5(2.9)[a]	159.1(2.9)[a]	>160	117.1(3.5)	133.1(2.3)	129.2(3.5)[a,b]
	108.3(6.8)[c]	154.5(5.5)[c]				110.3(4.6)[c]

[a] Average of the largest ϕ(H···M···H) angles. [b] Hydrogen atoms in equatorial positions. [c] Average of the diagonal ϕ(H···M···H) angles.

the increasing steric demand of the H, methyl and ethyl substituents, the metal–nitrogen distance shows a relative insensitivity toward the length and the number of the carbon chains connecting the donor nitrogen atoms. The ϕ(N–M–N) angles clearly reveal, however, that the nature of the hydrocarbon backbone affects the shielding caused by the coordinated ligand. While the angles formed by the N–M–N atoms vary within a narrow range in the case of ethylene diamines, they drop by 8 and 13° when the nitrogen atoms are bridged by two alkylene moieties as in hpip and dmpip. A reverse effect is seen in the case of 1,3-diaminopropane where insertion of a CH_2 unit increases the ϕ(N–M–N) angle by 6°. The separation of the nitrogen atoms closely follows the structural changes induced by the nature of the bridging alkylene units. The ϕ(N–M–N) and d(N···N) data indicate that the number and the size of the hydrocarbon chains may be an effective tool in varying the steric properties of the chelating diamines. However, in order to obtain a real estimate of the steric demand, the position of the outermost atoms that may interact with the neighbouring ligands should be considered.

Although the ϕ[H(N)···M···(N)H] angles are undoubtedly proportional to the shielding exercised by the ligand, a direct estimation of the ligand bulk from crystallographic data is troublesome because it is not obvious which of the angles may be accepted as a measure of bulkiness. Homopiperazine carrying only one hydrogen atom on each of the nitrogen atoms is a favourable exception because the H(N) atoms lay within 0.25 Å in the NMN plane and, therefore, the bulk of the coordinated ligand in square-planar complexes may be characterised by measuring the ϕ[H(N)···M···(N)H] angle. The situation is more complicated in the case of en and dap, where the hydrogen atoms of the primary amino groups are located on both sides of the MN(1)-N(2) plane. Here, two ϕ[H(N)···M···(N)H] angles involving hydrogen atoms on the same side as well as two diagonal angles can be measured. For our consideration, we selected the largest values of the four ϕ[H(N)···M···(N)H] data, and their average together with the estimated standard deviation are presented in the fourth line of Table 1. When the H(N) atoms were replaced by methyl groups, H(C) atoms approaching best the neighbouring ligands were selected to measure the ϕ[H(C)···M···(C)H] angles. The labels (N) and (C) are omitted in Table 1. We note that crystallographic data have been used to determine cone angles and ligand profile[21] but, to derive a relative ordering of steric bulkiness, a simpler analysis of the structural data seems to be satisfactory.

The data presented indicate that the selected diamines can roughly be divided into three groups. One can expect the smallest steric hindrance for ethylenediamine and homopiperazine. Replacement of the H(N) atoms by the more voluminous alkyl groups results in a sharp increase of the ligand bulk, as shown by the widening of the ϕ(H···M···H) angle, so the tetraalkyl derivatives should have a most pronounced influence on the composition of the reaction mixtures. *N*,*N*′-Dimethylpiperazine is supposed to occupy an intermediate position. However, the trend is not so straightforward in the case of diaminopropane. While the average of the largest angles suggests a bulkiness similar to that of dmpip, a survey of other structural features has revealed that this value is remarkably higher than the average of the diagonally measured angles (110.3°), in contrast to the behaviour of the en and tmen complexes [see second line of the ϕ(H···M···H) data]. This feature indicates that the orientation of the H(N) atoms in the dap complexes (at least in the solid state) is different from that in the M(en) compounds. An overview of the respective 3D structures has shown that this structural property is attributable to the chair conformation of the six-membered MN_2C_3 ring of dap complexes in which two H(N) atoms occupy axial positions on one side of the MN(1)N(2) plane while the other two H(N) atoms are oriented equatorially on the other side. Therefore, depending on the preferred conformation of the M(dap) moiety in solution, the steric requirement of the dap ligand may be less than expected on the basis of the largest ϕ(H···M···H) angle.

Estimation of the Bulkiness of Diamine Ligands by Computation

Lists of atomic coordinates available from single-crystal X-ray diffraction analysis or from theoretical molecular mechanics calculations can serve as input files for the program Solid-G. Besides the wide range of possibilities offered in analysing intramolecular interactions in a complex, the main advantage of the computational method is that it eliminates all the uncertainties associated with selecting angles and distances as indicators of bulkiness. In the simplest case, the solid angle Ω, the equivalent cone angle (*ECA*) and the *G* parameter can describe the steric bulk of a ligand. These data have been determined for the same set of complexes[19] that had been discussed in the preceding structural analysis and are presented in Table 2.

As expected, the values of the solid angle Ω show a steady increase on replacing the H(N) atoms by methyl or ethyl groups. In line with the prediction based on the ϕ(H···M···H) angles, the dmpip ligand occupies an intermediate position between en and tmen. There is a clear con-

Table 2. Steric bulkiness of diamine ligands as calculated by the program Solid-G.

	en	tmen	teen	hpip	dmpip[a]	dap
Ω(L)/sr[b]	4.18(0.09)	5.05(0.07)	5.73	4.61(0.03)	4.60	4.31(0.08)
ECA/°	140.37(2.88)	157.36(1.29)	169.85	149.19(0.53)	148.97(0.06)	143.37(1.44)
G^X(L)/%[c]	33.25(0.68)	40.19(0.55)	45.58	36.72(0.22)	36.62(0.03)	34.29(0.60)

[a] The methyl substituents of the propylene chain have been replaced by hydrogen atoms in molecules DANQAK and GOPJEA. [b] sr stands for steradian. [c] X indicates that the *G* values are computed from crystallographic coordinates.

flict, however, regarding the steric demand of homopiperazine. On the basis of crystallographic data, one can envisage that the spatial requirement of this diamine does not exceed that of en, which is the smallest in the whole series, while the calculated data predict a bulkiness comparable to that of dmpip. Further, the computed steric parameters indicate an increasing series of steric demand en < dap < dmpip, in contrast to the expected en < dap ≈ dmpip sequence deduced from the largest values of the ϕ(H···M···H) angles.

In summary, both the computed data obtained by the program Solid-G and the conclusions derived from crystallographic studies predict that the extent of the steric hindrances will follow the sequence en < dmpip < tmen < teen. Although the structural data and the calculations performed have not allowed a bottom-line conclusion to be drawn on the relative bulkiness in the cases of dmpip and hpip, both methods predict notably different steric behaviour of the selected diamine ligands, and these preliminary considerations formed the background of our experimental work.

Sterically Controlled Self-Assembly of Palladium Complexes

Typically, the synthesis of the self-assembled species was accomplished by adding **2** as a solid to an equivalent amount of **1** dissolved in water [N^N stands for diamines **a**–**f**; **a**: *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmen), **b**: *N*,*N*,*N*′,*N*′-tetraethylethylenediamine (teen), **c**: *N*,*N*′-dimethylpiperazine (dmpip), **d**: 1,3-diaminopropane (dap), **e**: homopiperazine (hpip), **f**: ethylenediamine (en)] [Equation (1)].

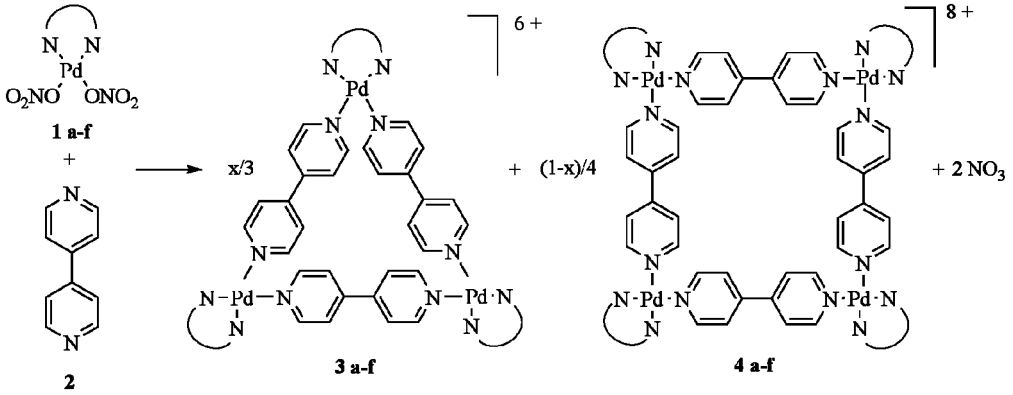
The progress of the reaction was indicated by the gradual discoloration of the initially bright yellow solutions and by dissolution of the otherwise water-insoluble reagent **2**. Characterisation of the isolated products rests on their NMR spectra, on their features related to their size such as diffusion coefficient and hydrodynamic radii determined by means of diffusion-ordered spectroscopy, and on studies of wide-angle X-ray diffraction recorded on solutions in equilibrium. Yields, and analytical and NMR spectroscopic data are presented in the Experimental Section.

Characterisation of the tmen Complexes by ^{1}H and DOSY NMR Spectroscopy

The ^{1}H NMR spectra of the isolated products show two sets of resonances with identical appearance due to the symmetric trimeric (**3**) and tetrameric (**4**) species.[9b,22] It follows that reliable identification of the molecular squares and triangles cannot be based on the interpretation of chemical shift differences. The molecular sizes of the symmetric trimeric and tetrameric complexes differ, and measurement of their diffusion coefficients (*D*) by NMR spectroscopy allows one to readily distinguish the various species in solution. Diffusion-ordered spectroscopy (DOSY) plays an increasingly important role in the identification of supramolecular species in solution owing to the straightforward two-dimensional representation of the components of the system.[12] The experimentally determined diffusion coefficients (*D*) allow the estimation of the effective hydrodynamic radii (*r*), which, in turn, depend on the number of tectons that were used to construct a selected constituent of the reaction mixture. The relationship between *D* and *r* is defined by the Stokes–Einstein equation[23] [Equation (2)] where *D* stands for Brownian diffusivity, k_B is the Boltzmann constant, η is the viscosity of the fluid and *r* is the hydrodynamic radius of the molecule assuming a spherical shape.

$$D = k_B T/6\pi\eta r \quad (2)$$

The primary experimental data (*D*) and the calculated approximate spherical hydrodynamic radii of aggregates **3** and **4** (*r*) are collected in Table 3. The success of the DOSY experiments was largely dependent on the fact that the changes in the composition (triangle/square) of the mixture by the temperature or concentration were much slower than the NMR experiments. Additionally, a series of ^{1}H NMR spectra recorded at different temperatures and concentrations allowed one to make the same assignment of resonances (see below).



(1)

Table 3. Diffusion coefficients and calculated hydrodynamic radii of self-assembled $[Pd(N–N)(4,4'\text{-bpy})]_n^{2n+}$ complex cations (n = 3 or 4).

Chelating ligand	Diffusion coefficients/$\times 10^{-10}$ m^2 s^{-1}		Hydrodynamic radii/Å	
	Square, **4**	Triangle, **3**	Square, **4**	Triangle, **3**
tmen (**a**)	2.5 ± 0.1	2.9 ± 0.1	7.7 ± 0.3	6.7 ± 0.3
teen (**b**)	2.2 ± 0.1	2.4 ± 0.1	8.8 ± 0.4	8.0 ± 0.3
dmpip (**c**)	2.2 ± 0.1	2.6 ± 0.1	8.8 ± 0.4	7.4 ± 0.3
dap (**d**)	2.4 ± 0.1	2.8 ± 0.1	8.0 ± 0.3	6.9 ± 0.2
hpip (**e**)	2.4 ± 0.1	3.0 ± 0.2	8.0 ± 0.3	6.4 ± 0.4
en (**f**)	2.7 ± 0.1	3.6 ± 0.2	7.2 ± 0.2	5.4 ± 0.3

The ^{1}H DOSY spectrum of a typical two-component mixture formed in the reaction of **1a** with **2** is presented in Figure 1. The resonances of the conventional (1D) ^{1}H NMR spectrum are separated according to the diffusion rate of the molecules present in the solution, and, in the given case, they form two sets of resonances at $D = 2.5 \times 10^{-10}$ m^{2}s^{-1}and $D = 2.9 \times 10^{-10}$ m^{2}s^{-1}, respectively (Table 3, line 1). As the major component is characterised by the smaller diffusion coefficient, and, consequently, by the larger hydrodynamic radius, the DOSY spectrum provides us with direct evidence for its identification as the tetrameric species **4a**, while resonances of the minor constituent have been ascribed to the trimeric aggregate **3a**. The calculated hydrodynamic radii are in good agreement with the size determined from the molecular structure of the crystallographically characterised **3a** and **4a** adducts.[24]

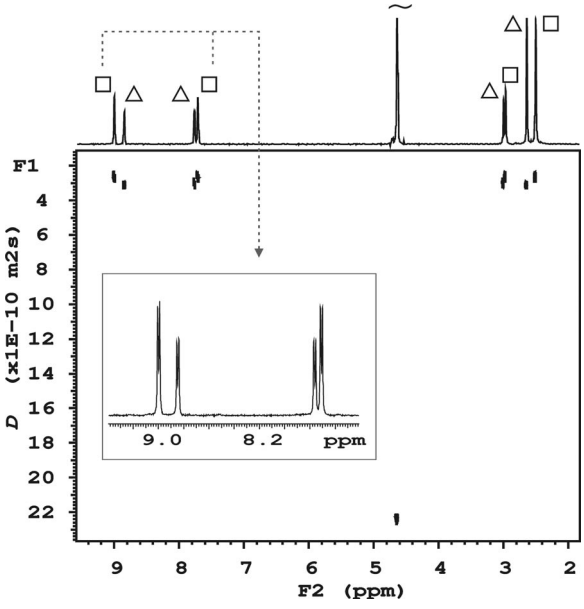


Figure 1. ^{1}H DOSY spectrum showing the mixture of **3a** and **4a** formed in the reaction of $[Pd(tmen)](NO_3)_2$ and 4,4′-bpy.

In line with the observations of Mizuno et al.,[24] the equilibrium composition of the solutions in D_2O shows a strong dependence on the tecton concentration (Figure 2). At a tecton concentration of 101 mM, the molar ratio of the tetrameric (**4a**) and trimeric (**3a**) species amounts to 2.6:1, but it drops to 0.86:1 when the concentration is decreased to 7 mM. In the most diluted solution (3.5 mM), new resonances of low intensity could be detected that have been ascribed to less symmetrical components whose organisation into a closed geometrical form was not completed.

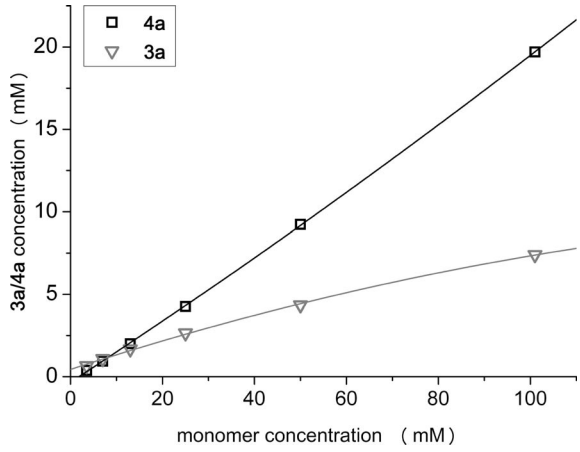


Figure 2. Molar concentrations of the square and triangle species, $[Pd(tmen)(4,4'\text{-bpy})]_n^{2n+}$ (n = 3, 4), at different tecton concentrations (T = 25 °C).

Raising the temperature by small increments from 25 °C to 50 °C ([tecton] = 50 mM) results in the gradual decrease of the major (tetrameric) component from 68 to 56% with the simultaneous enrichment of the minor (trimeric) constituent. Upon cooling the sample, the molar ratio of the two components returns to the original value at that temperature without showing any sign of hysteresis or decomposition. The trend detected by the temperature-dependent interconversion of the two components is in line with the preferential formation of the tetrameric (square) component over the more strained trimeric species when a 90° corner element is combined with a rigid linear bridging ligand and supports the identification of the major component as a molecular square.

Characterisation of the Trimer/Tetramer Equilibrium by Solution X-ray Diffraction Studies

Studying the constituents formed in the $[Pd(tmen)]^{2+}$/4,4′-bpy system, we have observed that the isolated product is outstandingly soluble in water, and solutions with tecton concentrations exceeding 0.5 M can be prepared. This feature has offered a direct observation and characterisation of the $[Pd(tmen)(4,4'\text{-bpy})]_n^{2n+}$ constituents (n = 3, 4) in solution by using wide-angle X-ray diffraction as an experi-

mental technique. This method has been typically used for structural studies of liquids and solutions of small molecules. Recently, the technique of structural characterisation of supramolecular species in solution using wide-angle X-ray diffraction has been described.[25] To the best of our knowledge, no attempts have been made to observe a supramolecular trimer/tetramer equilibrium by way of X-ray diffraction on solutions. The experimental results are summarised in the forthcoming section.

The measured structure functions $kh(k)$ are compared to the calculated contributions from the solvent in Figure 3. The theoretical contributions were calculated on the basis of the equations given earlier.[25] The total solvent contribution to the structure function of the solution was subtracted, and the resultant difference curves were compared to the intramolecular contributions of the two complexes, triangle and square. The intramolecular contributions of the complexes were calculated using the structural parameters obtained from single-crystal X-ray diffraction.[24] The similarity of the calculated and measured scattering curve for the square is remarkable considering that interactions between the molecular assembly and the solvent were not taken into account. This observation suggests that the solution contains mostly the square complex, but the triangle is also present in solution. Because of the complexity of this system, further analysis of the interactions between the molecular assembly and the solvent was not possible.

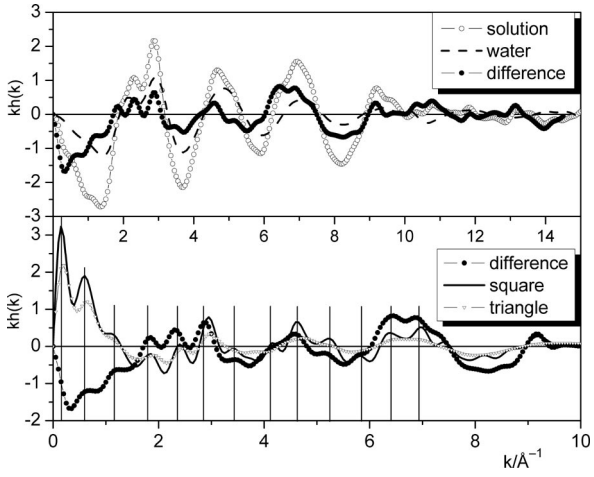


Figure 3. Structure functions $h(k)$ multiplied by k for 0.52 M aqueous solution. The difference curve (circles) was obtained by subtracting the total solvent contribution (dashed) from the measured structure function (open circles). This difference curve (circles) is in good agreement with the theoretical intramolecular contributions of the square complex (line) but shows less good agreement with the theoretical intramolecular contributions of the triangle (open down triangle). For ease of comparison, the main peaks are marked with vertical lines.

The pair-correlation functions [$g(r)$] are shown in Figure 4. A visual inspection of the radial distribution functions indicates that they are composite, and no peaks can be uniquely assigned to a specific interaction. The first two peaks in the pair correlation function are centred at about 1.20 and about 2.05 Å and arise from the intramolecular contributions from the complex. The solvent and anion interactions are of short range (< 3 Å) and most likely overlap to form these peaks.

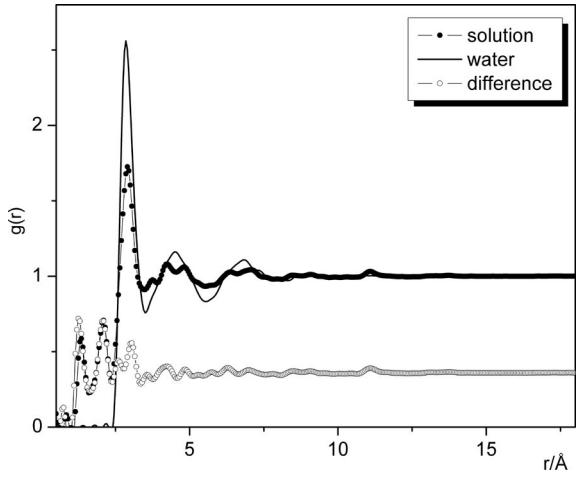


Figure 4. Pair-correlation functions [$g(r)$] for 0.52 M aqueous solution: solution (circles), solvent (line) and the difference between solution and solvent contribution.

The experimental palladium–palladium pair-correlation functions have been calculated and fitted to modelled pair-correlation functions containing a sum of Gauss functions.[25] The palladium–palladium distances (r), mean square deviations (σ) and coordination numbers (n) were obtained. Parameters obtained are given in Table 4.

Table 4. The palladium–palladium distances (r), mean square deviations (σ) and coordination numbers (n) obtained.

r/Å	σ/Å	n
11.20(0.01)	0.19(0.01)	2.19(0.10)
15.55(0.03)	0.23(0.03)	0.82(0.05)

As expected, two palladium–palladium interactions are observed in the pair-correlation function. The shorter distance appears at 11.20(0.01) Å corresponding to the palladium–palladium distances along the sides of the square and triangle. These interactions overlap and are difficult to resolve. The longer distance at 15.55(0.03) Å belongs to the diagonal of the square. The number of palladium–palladium interactions that give rise to these peaks, hereafter referred to as coordination number (n), was determined to be 2.19(0.1) and 0.82(0.05) for the peaks at 11.2 and 15.5 Å, respectively. If the solution contained only the square, the coordination number corresponding to the longer (diagonal) palladium–palladium interaction would be about 1. The finding that the coordination number is < 1 suggests that approximately 80% of the palladium ions is involved in squares and the remaining 20% in triangles. These data coincide well with the distribution of the tectons in a ratio of 83:17 as observed in the ^{1}H NMR spectrum of the same solution. The pair-correlation functions in the $r^2[g(r) - 1]$

representation are shown in Figure 5. The contributions arising from Pd···C and Pd···N interactions are also shown, as they were obtained supposing the above-obtained ratio for square/triangle.

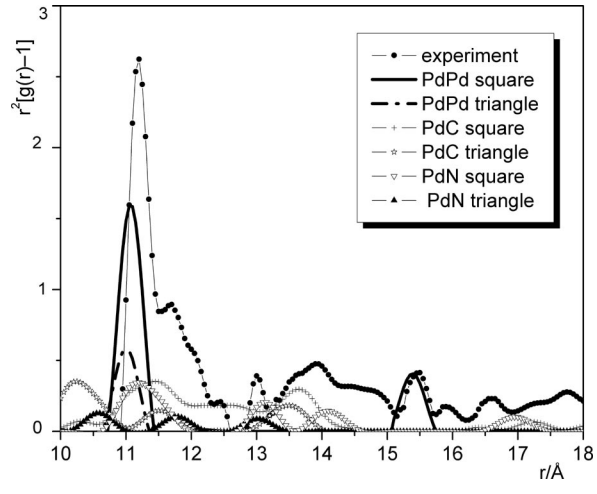


Figure 5. Experimental pair-correlation functions $\{r^2[g(r) - 1]\}$ for 0.52 M complex in aqueous solution and calculated pair-correlation functions for different contributions arising from square and triangle.

Comparison of the experimental and theoretical peaks suggests that the square retains its shape in solution. However, the peaks corresponding to the palladium–palladium distances are a little longer than those observed in the solid state. Taken together, these data suggest that the square, while shape-persistent, is not as rigid in solution as in the crystalline state. Most likely, the square is rather flexible in solution, and the experimental data presented reflect the average of the observed structural parameters.

We note that we have detected the signs of a new, highly symmetrical constituent in the ^{1}H NMR spectrum of the most concentrated solutions (about 0.5 M). The available data do not allow an unequivocal structural characterisation of this species, but the systematic shift of the resonances in the aromatic region [the multiplets attributed to the trimer (δ = 8.91 and 7.82 ppm) are surrounded by those of the tetramer (δ = 9.06 and 7.77 ppm) which, in turn, are flanked by the new resonances (δ = 9.08 and 7.73 ppm)] suggests that the extremely high tecton concentration results in the formation of a self-assembled species whose nuclearity may be higher than four. We have not attempted to further characterise this product.

In summary, the emergence of the trimeric tmen complex is in line with the remarkably differing steric requirements of the tmen and en ligands as predicted by the crystallographic data as well as by the calculated *G* parameter. DOSY and wide-angle X-ray diffraction have proved to be efficient tools in the identification of supramolecular species. Simultaneous application of these techniques can provide direct experimental evidence regarding the nuclearity of the constituents in solutions.

Compositions in Equilibrium with teen, dap, dmpip, hpip and en as Chelating Ligands

The self-assembled aggregates studied here possess rather dissimilar solubility in water. While the highest concentration of the products formed with teen and hpip as chelating ligands approaches that of the tmen adducts, we experienced a rather limited solubility (about 20 mM) with dap and dmpip. In order to compare the distribution of the tectons under identical conditions, solutions of 13 mM tecton concentration were prepared in all cases. Diffusion-ordered spectroscopy was used as a major tool for the identification of the components observed in the ^{1}H NMR spectra. The diffusion coefficients and the hydrodynamic radii of the self-assembled species are presented in Table 3.

Like with tmen, the interaction of the tetraethylethylenediamine complex **1b** with **2** ends up with the formation of a two-component reaction mixture with a distribution of tectons between the major and minor constituents in a ratio of about 4.6:1 (25 °C, [tecton] = 13 mM). The change of the proportion of the two complexes upon varying the concentration indicated, however, that it is the trimeric species that is the predominant product of the assembly process in this case. The percentage of the tectons involved in the construction of the trinuclear aggregate exceeds 70% even at high (50 mM) concentration and amounts to 87% at 3.5 mM. Variable-temperature ^{1}H NMR experiments have delivered further support for identifying the major component as a trimer. We have found that a stepwise increase of the temperature from 25 to 50 °C resulted in a gradual enrichment of the major product whose proportion rose from 75 to 82%. Finally, DOSY experiments revealed that the prevailing constituent is characterised by the larger diffusion coefficient, which confirms the identification of this compound as a trimeric species.

It is evident from the experimental data presented that the size of the corner ligand exercises a decisive effect on the self-assembly of macrocyclic molecules, and bulky diamines can establish square/triangle equilibriums shifted to the predominant formation of the smaller, although energetically less advantageous, trimeric constituents. The notably high proportions of the trimeric species agree well with the observation that teen has the largest *G* parameter in the series of chelating ligands studied here.

Dimethylpiperazine is a sterically less demanding ligand than tetramethylethylenediamine. When dmpip binds to metal centres as a chelating agent, the ϕ(N–M–N) angles are remarkably smaller (72.6°) than those in the tmen complexes (85.7°). The reduced bulkiness is reflected also by the narrower ϕ(H···M···H) angle (133 vs. 159°), and the value of the *G* parameter takes an intermediate position between those of en and tmen. Therefore, a shift of the square/triangle equilibrium toward the tetramer is expected. In line with the structural data, the major component in equilibrium has been proven to possess the smaller diffusion coefficient and has been identified as a tetrameric species. At 25 °C and 13 mM total concentration, the [Pd(dmpip)(4,4′-bpy)]$^{2+}$ unit is distributed between the square and triangle

species in a ratio of 83:17, as indicated by the integrals of the respective resonances of the ^{1}H NMR spectra.

As pointed out above, the structural data did not give an unequivocal prediction regarding the steric property of 1,3-diaminopropane. Based on the largest value of the ϕ(H···N···H) angles, dap can be considered as a steric counterpart of dmpip. The *G* parameter suggests, however, that the bulkiness of dap is reminiscent of that of en rather than the steric bulk of dmpip. The analysis of the ^{1}H NMR spectra supported by the experiments carried out under diffusion-controlled conditions has shown that the interaction of $[Pd(dap)]^{2+}$ with 4,4′-bpy results in a tecton distribution closely resembling that observed with dmpip. The major component incorporating 84% of the building elements has been identified as a molecular square being in equilibrium with the trimeric aggregate $[Pd(dap)(4,4'\text{-bpy})]_3^{6+}$. The almost identical trimer/tetramer ratio observed with dmpip and dap ligands is noteworthy. It may indicate that the chair conformation of the six-membered MN_2C_3 ring observed in the solid state is favoured energetically rather than being a result of packing forces, and this conformation prevails in solution as well. Consequently, the largest value of the ϕ(H···N···H) angles determined by H(N) atoms in equatorial positions reflects more accurately the steric demand of the dap ligand than those measured diagonally between hydrogen atoms in equatorial and axial positions of which the latter cannot be involved in repulsive interactions with the neighbouring ligands.

A comparison of the crystallographic and computed data of homopiperazine (Tables 1 and 2) reveals an even more contradictory assessment of the steric properties of this ligand. Judging by the relatively small ϕ(H···M···H) angle (117.1°), one may expect to assemble a sterically noncongested multimetallic complex with the exclusive or predominant formation of the tetrameric aggregate. The *G* parameter of hpip is, however, nearly equal to that of dmpip, which suggests an equilibrium mixture with a considerable proportion of trimeric species. The ^{1}H NMR spectra do indicate the presence of a minor product although in much lower yield (< 5%) than expected on the basis of our computational study. Further, DOSY experiments gave evidence for the formation of two voluminous constituents of which the minor one diffuses faster and is thought to be a trimeric species.

The remarkable disagreement between the predictions based on the crystallographic data and the computed *G* parameter deserves attention. We believe that the dissimilar extent of bulkiness obtained by the two methods is attributable to the different approach one follows when the numerical values of ϕ(H···M···H) angles and *G* parameters are determined. In the former case, selection of the atoms determining the required angles is based on a hypothesis. In favourable instances (if the hypothesis is right), one can identify the atoms whose interaction with neighbouring ligands governs the intramolecular repulsive forces and the angles determined by them, and the metal centre may reveal the right sequence of steric demand for a series of ligands. When doing so, we unintentionally neglect the presence of atoms that are considered as unimportant in the emergence of steric effects.

The computation of the *G* parameter is based, however, on a different approach. In this case we figure out the solid angle of a ligand, which, in turn, contains the contribution of all the atoms not considering if a particular moiety of the molecule can affect the steric hindrance. It seems reasonable to think that, in a square-planar complex, it is the H(N) atoms that are primarily involved in steric interactions rather than the ethylene and propylene hydrocarbon chains that are remote from the neighbouring ligands but contribute decisively to the solid angle and all data derived from it. Therefore, we assume that the bulkiness assessed on the basis of the ϕ(H···M···H) angles may offer a better approximation of the real steric demand of hpip than the *G* parameter that is believed to be overestimated for this diamine. We believe that the contradictory assessment of the ligand bulk for hpip may be ascribed to the attempt to characterise a complex feature like steric behaviour by a single numeral.

The appearance of a relatively large amount of the trimeric product, $[Pd(hpip)(4,4'\text{-bpy})]_3^{6+}$, was unexpected because the nearly identical values of the ϕ(H···M···H) angles of the hpip and en ligands suggest very similar steric properties of their complexes. Moreover, the $[Pd(en)]^{2+}$ tecton combined with the rigid 4,4′-bpy has been reported to form the molecular square quantitatively.[1a,1d] Therefore, it seemed worth examining if any minor component in the reaction of **1f** with **2** can be detected.

The top part of Figure 6 shows the ^{1}H NMR spectrum of a reaction product (13 mM, 25 °C) isolated from the interaction of **1f** with 1 equiv. of **2**. Besides the known resonances attributable to the molecular square **4f**, resonances of low intensity clearly show up both in the aromatic and in the aliphatic regions. The ratio of the peak intensities has

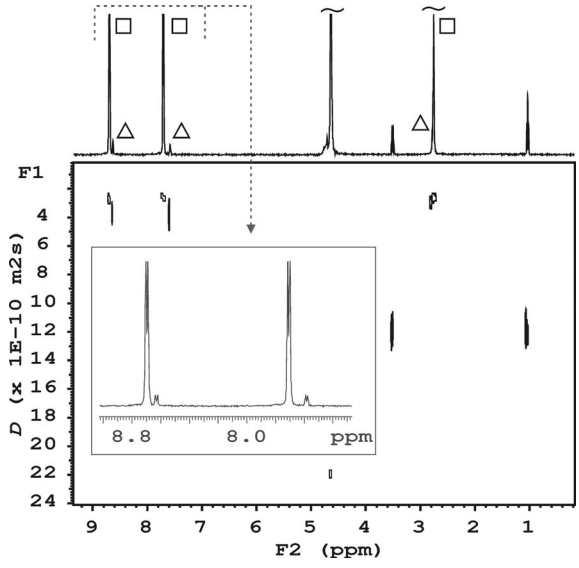


Figure 6. DOSY spectrum of the macrocycles formed in the interaction of $[Pd(en)](NO_3)_2$ and 4,4′-bpy. Traces of ethanol are present.

Table 5. Selected steric parameters of the **1a**–**f** complex cations and distribution of the tectons (%) between the trimeric (**3**) and tetrameric (**4**) aggregates (25 °C, [tecton] = 13 mM).

	en	tmen	teen	hpip	dmpip	dap
ϕ(H···M···H)/°	114.5(2.9)	159.1(2.9)	>160	117.1(3.5)	133.1(2.3)	129.2(3.5)
G^X(L)/%	33.25(0.68)	40.19(0.55)	45.58	36.72(0.22)	36.62(0.03)	34.29(0.60)
Triangle/square	94:6	61:39	18:82	96:4	83:17	84:16

allowed us to estimate the minor component to involve about 6% of the tectons. A DOSY experiment has readily identified this species as an aggregate whose diffusion coefficient exceeds that of the major constituent but is still distinctive for large assemblies.

This observation together with the varying percentage of the tectons in the trimeric and tetrameric constituents at various tecton concentrations (c = 37 mM, triangle/square = 4:100; c = 6 mM, triangle/square = 8:100 at 25 °C) and also the enrichment of this species in solutions at elevated temperatures (25 °C, triangle/square = 4:100; 80 °C, triangle/square = 10:100 at c = 37 mM) have allowed us to identify the minor constituent as the trimeric **3f**. Although the amount of the trinuclear aggregate is really small, this observation emphasises that it is really difficult to find corner elements that lead to the formation of a single self-assembled species. To the best of our knowledge, this is the first instance that the trimeric $[Pd(en)(4,4'\text{-bpy})]_3^{6+}$ cation has been identified.

Table 5 gives a summary of our basic findings. At 25 °C and 13 mM tecton concentration, a triangle/square equilibrium is established even with ligands possessing the smallest ϕ(H···M···H) angles and G parameters. The proportion of the tectons incorporated in the trimeric species varies in a wide range (4–82%); thus, depending on the ligand bulk, either the tetramer or the trimer can be observed as the major constituent. These observations are in line with the importance of the steric effects in determining the chemical and physical properties of organometallic systems and may help to choose ligands for a self-assembly reaction most suitable for the desired aggregation.

Conclusions

We have studied the influence of the steric bulk of diamine ligands on the distribution of tectons between the trimeric and tetrameric species formed in the interaction of $[Pd(N^{\frown}N)](NO_3)_2$ complexes with 4,4′-bpy. In order to estimate the steric requirements of selected chelating amines, the ϕ(H···M···H) angles have been taken as a potential measure of ligand bulk. As an alternative way, atomic coordinates were used to compute the steric parameters of the same diamines. Both methods suggest the sequence of bulkiness teen > tmen > dmpip > en, but additional consideration had to be made in the case of hpip and dap to rationalise the steric behaviour of these diamines in the light of their specific structural features. The proportion of the tectons incorporated in the energetically less advantageous trimeric constituent has been found to follow the sequence of increasing steric demand of the chelating diamines. All reaction parameters that may influence the position of the trimer/tetramer equilibrium such as concentration, temperature, solvent, anion and the electronic feature of the ligands have been kept constant. Therefore, the experimental results presented here are attributable with certainty to the dissimilar bulkiness of the diamines and are clear demonstrations of the potential extent of steric crowdedness in the process of self-assembly. The systematic study of steric effects has allowed observation and identification of the trimeric $[Pd(en)(4,4'\text{-bpy})]_3^{6+}$ cation for the first time.

Diffusion-ordered spectroscopy has proved to be an efficient method for the identification of self-assembled complexes of various molecular sizes. The observation of the trimeric and tetrameric tmen complexes in solution by using wide-angle X-ray diffraction offers a new tool for the characterisation of mixtures of highly symmetrical multimetallic complexes.

Synthesis and studies of new ligands capable of size-selective interaction with metal complexes are in progress in our laboratory.

Experimental Section

General: NMR spectra were recorded with a 400-MHz (for ^{1}H) Varian Inova spectrometer equipped with a Varian 5-mm ^{1}H-^{19}F/$\{^{15}$N-^{31}P$\}$ Z-gradient indirect-detection probe. ^{1}H chemical shifts were referenced to the residual solvent signal (δ_{HOD} = 4.64 ppm). 99.95% perdeuterated D_2O was purchased from Merck GmbH, Germany. The ^{1}H-DOSY experiments were carried out in a 2-mm capillary placed in a 3-mm tube at 25 °C to minimise convection effects. A Performa I gradient amplifier was used with a 20 Gauss cm^{-1} maximum gradient capability. The gradient strength was calibrated by using 5% (w/w) sucrose in D_2O at 25 °C (D = 5.22×10^{-10} m^2 s^{-1}). The bipolar pulse-pair stimulated-echo (Dbppste) pulse sequence was used for acquiring diffusion data with 50 ms diffusion delay, 16 squared increments for gradient levels and 16 transients. The Varian DOSY package was used for the processing. A water (D_2O) viscosity of η = 1.132 mPa·s was used for the calculation of the hydrodynamic radii at 25 °C.

X-ray Diffraction: The X-ray diffraction measurement was carried out on a 0.52 M solution of $[Pd(tmen)(bpy)](NO_3)_2$ in D_2O (ρ = 1.18 g cm^{-3}) at room temperature (24 ± 1 °C) using a Philips X'Pert goniometer in a vertical Bragg–Brentano geometry with a pyrographite monochromator in the scattered beam and proportional detector [Mo-K_α radiation (λ = 0.7107 Å)]. Quartz capillaries (1.5 mm diameter, 0.01 mm wall thickness) were applied as the liquid sample holder. The scattering angle range of measurement spanned over 1.28° ≤ 2Θ ≤ 130.2°, corresponding to a range of 0.2 Å^{-1} ≤ k ≤ 16.06 Å^{-1} of the scattering variable $k = (4\pi/\lambda)\sin\Theta$. Over 100000 counts were collected at each angle in $\Delta k \approx 0.05$ Å^{-1} steps.

Preparations: All chemicals were purchased from commercial sources and used as received. The intermediate $[Pd(N^{\frown}N)Cl_2]$ complexes[26] and the $[Pd(en)(4,4'\text{-bpy})]_4(NO_3)_8$ tetramer[1a] were prepared as described. For the syntheses of $[Pd(N^{\frown}N)(NO_3)_2]$ complexes, an established procedure[27] was used with minor modifications. All the dinitrates were isolated, and their purity was checked by ^{1}H NMR spectroscopy. The IR spectra of **1a**–**f** showed that the nitrate ions were coordinated to the metal centre.[28] To the best of our knowledge, compounds **1c** and **1e** are new; their preparations and analytical data are given below.

[Pd(dmpip)(NO$_3$)$_2$] (1c): [Pd(dmpip)Cl$_2$] (130 mg, 0.446 mmol) was added to a stirred solution of $AgNO_3$ (151.3 mg, 0.891 mmol) in water (9 mL) acidified with two drops of nitric acid (1 M). The reaction mixture was stirred at room temperature overnight. The filtered solution was concentrated in a Rotavapor to yield a yellow crystalline solid that was dried with P_2O_5 under vacuum. Yield: 151 mg (98%). ^{1}H NMR: δ = 3.68–3.84 (m, 4 H, CH_2), 2.30–2.46 (m, 4 H, CH_2), 2.23 (s, 6 H, CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 1500, 1476 (sh), 1459 (sh), 1384, 1281, 1263, 994, 795 cm^{-1}. $C_6H_{14}N_4O_6Pd$ (344.59): calcd. C 20.91, H 4.10, N 16.26; found C 20.44, H 4.06, N 16.13.

[Pd(hpip)(NO$_3$)$_2$] (1e): This complex was prepared analogously to compound **1c**. Reaction of $AgNO_3$ (176.0 mg, 1.036 mmol) with [Pd(hpip)Cl$_2$] (143.7 mg, 0.518 mmol) in water (10 mL) acidified with two drops of nitric acid (1 M) allowed the isolation of **1e**. Yield: 167 mg (97%). ^{1}H NMR: δ = 3.33–3.51 (overlapping m, 4 H), 2.53–2.65 (m, 2 H), 2.41–2.53 (m, 2 H), 2.13–2.26 (br. m, 1 H), 1.91–2.10 (m, 1 H) ppm. IR (KBr): $\tilde{\nu}$ = 3213, 1498, 1384, 1281, 1006, 990 cm^{-1}. $C_5H_{12}N_4O_6Pd$ (330.57): calcd. C 18.17, H 3.66, N 16.95; found C 18.61, H 3.63, N 17.05.

Self-Assembly of Compounds 3a–3f and 4a–4f: The reaction of **1a** with **2** is described as a typical procedure.[1a] 4,4′-bpy (168 mg, 1.079 mmol) was added to [Pd(tmen)](NO$_3$)$_2$ (374 mg, 1.079 mmol) dissolved in water (2 mL) at room temperature. The reaction mixture was stirred for 15 min, whilst the bright yellow solution turned almost colourless. Addition of ethanol resulted in a pale yellow precipitate that was filtered off and washed with ethanol and diethyl ether. The microcrystalline solid was dried with P_2O_5 in vacuo. Yields, ^{1}H NMR spectroscopic data for the individual components **3** and **4** (D$_2$O, 25 °C, 13 mm) and elemental analysis data for the self-assembled products are summarised below. As shown by the analytical data, the experimental conditions proved to be insufficient to remove all of the water of crystallisation. A good agreement between the expected and experimental data was achieved if the presence of 1 or 1.5 equiv. of water per [Pd(N–N)(4,4′-bpy)](NO$_3$)$_2$ tecton was assumed. Chelating ligand: tmen. Yield: 522 mg (91%). ^{1}H NMR: **3a**: δ = 8.80–8.88 (m, 4 H), 7.74–7.80 (m, 4 H), 3.00 (s, 4 H, CH_2), 2.64 (s, 12 H, CH_3); **4a**: δ = 8.95–9.05 (m, 4 H), 7.64–7.74 (m, 4 H), 2.96 (s, 4 H, CH_2), 2.50 (s, 12 H, CH_3) ppm. $(C_{16}H_{24}N_6O_6Pd\cdot 1.5H_2O)_n$ (529.82)$_n$: calcd. C 36.27, H 5.14, N 15.86; found C 36.31, H 5.30, N 15.70. Complexes **1c**–**1f** reacted analogously with **2**. Chelating ligand: dmpip. Yield: 155 mg (84%). ^{1}H NMR: **3c**: δ = 8.75–8.79 (m), 7.64–7.68 (m), 3.95–4.00 (br. overlapping m, CH_2), 2.57–2.74 (br. overlapping m, CH_2), 2.33 (s, 3 H, CH_3); **4c**: δ = 8.88–8.96 (m), 7.74–7.81 (m), 3.86–3.95 (br. m, CH_2), 2.57–2.74 (br. overlapping m, CH_2), 2.13 (s, 3 H, CH_3) ppm. $(C_{16}H_{22}N_6O_6Pd\cdot 1.5H_2O)_n$ (527.80)$_n$: calcd. C 36.41, H 4.77, N 15.92; found C 36.81, H 4.84, N 15.92. Chelating ligand: dap. Yield: 107 mg (85%). ^{1}H NMR: **3d**: δ = 8.63–8.67 (m, 4 H), 7.57–7.61 (m, 4 H), 2.62–2.66 (overlapping m, CH_2), 1.71–1.81 (overlapping m, CH_2); **4d**: δ = 8.73–8.78 (m, 4 H), 7.69–7.73 (m, 4 H), 2.58–2.63 (overlapping m, CH_2), 1.71–1.81 (overlapping m, CH_2) ppm. $(C_{13}H_{18}N_6O_6Pd\cdot H_2O)_n$ (478.74)$_n$: calcd. C 32.62, H 4.21, N 17.55; found C 32.71, H 4.19, N 17.17. Chelating ligand: hpip. Yield: 160 mg (89%). ^{1}H NMR: **3e**: δ = 8.63–8.68 (m, 4 H), 7.58–7.62 (m, 4 H), 3.51–3.68 (overlapping m, CH_2), 2.75–2.91 (overlapping m, CH_2), 2.07–2.34 (overlapping m, CH_2); **4e**: δ = 8.69–8.77 (m, 4 H), 7.70–7.77 (m, 4 H), 3.51–3.68 (overlapping m, 4 H, CH_2), 2.75–2.91 (overlapping m, 4 H, CH_2), 2.07–2.34 (overlapping m, 2 H, CH_2) ppm. $(C_{15}H_{20}N_6O_6Pd\cdot 1.5H_2O)_n$ (513.78)$_n$: calcd. C 35.07, H 4.51, N 16.36; found C 35.27, H 4.50, N 15.91. Chelating ligand: en. ^{1}H NMR: **3f**: δ = 8.61–8.64 (m, 4 H), 7.56–7.60 (m, 4 H), 2.79 (s, 4 H) ppm. We found that **1b** and **2** gave an intractable oily product in water. Because of the reasonably good solubility of **1b** in CH_2Cl_2, this reaction can be performed in a purely organic solvent. 4,4′-bpy (24 mg, 0.154 mmol) was administered to a solution of [Pd(teen)](NO$_3$)$_2$ (62 mg, 0.154 mmol) dissolved in CH_2Cl_2 (30 mL) at room temperature. In a few seconds, a pale yellow solid precipitated. Concentration of the reaction mixture to dryness allowed the isolation of a mixture of **3b** and **4b**. Yield: 83 mg (92%). ^{1}H NMR: **3b**: δ = 8.80–8.85 (m, 4 H), 7.67–7.75 (overlapping m), 2.96–3.11 (overlapping m, CH_2), 2.79–2.95 (overlapping m, CH_2), 2.65–2.76 (overlapping m, CH_2), 1.44 (t, $^3J_{H,H}$ = 7.3 Hz, 12 H, CH_3); **4b**: δ = 8.96–9.01 (m, 4 H), 7.67–7.75 (overlapping m), 2.96–3.11 (overlapping m, CH_2), 2.79–2.95 (overlapping m, CH_2), 2.65–2.76 (overlapping m, CH_2), 1.39 (t, $^3J_{H,H}$ = 6.8 Hz, 12 H, CH_3) ppm. $(C_{20}H_{32}N_6O_6Pd\cdot 1.5H_2O)_n$ (585.93)$_n$: calcd. C 41.00, H 6.02, N 14.34; found C 41.05, H 6.13, N 14.20.

Acknowledgments

We thank the Hungarian Research Fund (OTKA T047321) for funding of this work. Financial support from the National Office for Research and Technology through the projects NAP VENEUS05 OMFB-00650/2005, Hungarian GVOP-3.2.1.-2004-04-0210/3.0 and MU-00338/2003 is gratefully acknowledged. We are indebted to Professor I. A. Guzei (University of Wisconsin, Madison, USA) for making the program Solid-G available to us, and for valuable discussion.

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Received: November 6, 2007
Published Online: February 13, 2008

