

A new class of self-assembly multinuclear Pt(II) coordination cages by a modular approach

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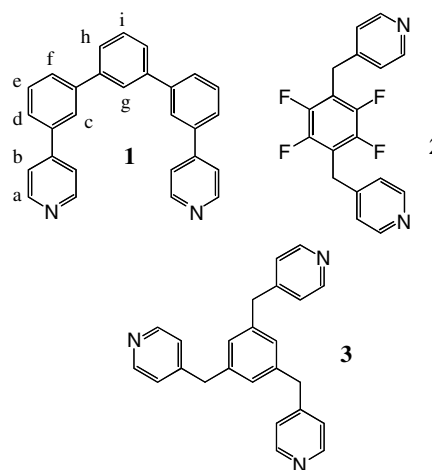
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Abstract—The formation of three examples of a new class of self-assembly Pt(II) cage molecules of general formula $[Pt_m(\text{ligand})_n](\text{NO}_3)_{2m}$ is achieved from Pt(II) and ligands. The compounds are observed in solution state and confirmed from the similarity of their proton NMR behavior as compared with that of reported Pd(II) compounds of the formula $[Pd_m(\text{ligand})_n](\text{NO}_3)_{2m}$. © 2006 Elsevier Ltd. All rights reserved.

Self-assembly chemistry of cis-protected square planar Pd(II) and a suitable ligand has been considerably explored in order to obtain multinuclear cage compounds.¹ A typical procedure for such synthesis is the combination of mononuclear cis-protected Pd(II), for example, *cis*-Pd(en)(NO₃)₂ with the required amount of appropriate non-chelating multi-dentate ligand under suitable reaction conditions. The self-assembly so obtained may be formulated as $[{\textit{cis}}\text{-Pd}(\text{en})\}_x(\text{ligand})_y](\text{NO}_3)_{2x}$. Similar ligands are frequently complexed with mononuclear cis-protected Pt(II).² Also, acyclic polynuclear Pt(II) compounds, where three out of the four sites of each metal center is already complexed are combined with multi-dentate ligands to obtain cyclic assemblies.² In contrast, only recently have a few reports^{3,4} appeared on the use of Pd(II) as a metal center to obtain supramolecular structures having the formula $[Pd_m(\text{ligand})_n](\text{NO}_3)_{2m}$. We could not find any examples of multinuclear complexes prepared simply from Pt(II) and suitable ligands for the construction of architectures having the formula $[Pt_m(\text{ligand})_n](\text{NO}_3)_{2m}$. Therefore, we chose a few reported compounds³ of general formula $[Pd_m(\text{ligand})_n](\text{NO}_3)_{2m}$ and directed our efforts to obtain related Pt(II)-containing assemblies using Pt(II) and the ligand.

The ligands³ used in this study **1**, **2**, and **3** are shown in Scheme 1 and the corresponding multinuclear Pt(II) complexes **4a**, **5a**, and **6a** observed in the solution state

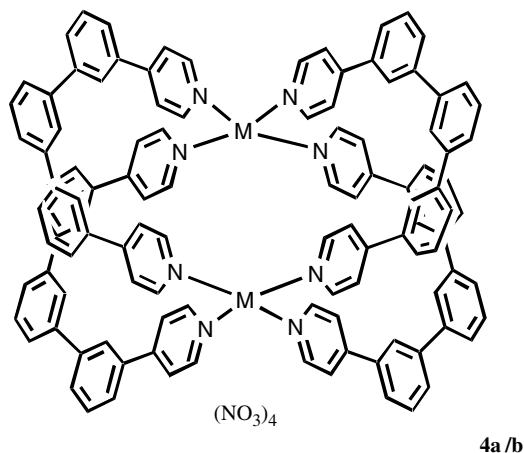


Scheme 1. Ligands 1–3.

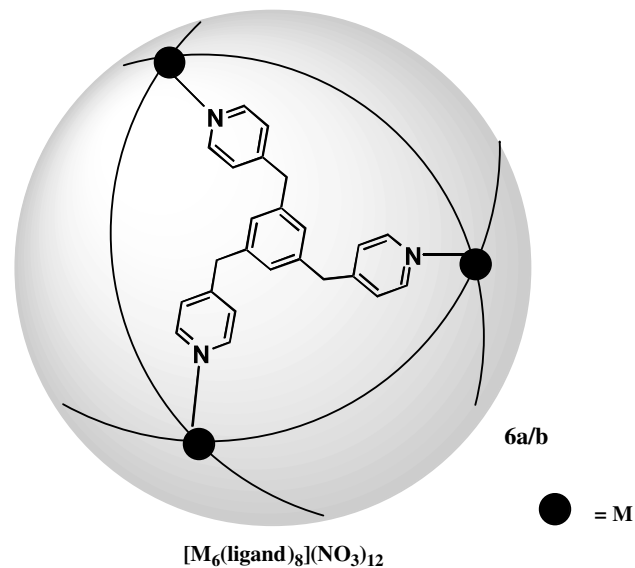
are depicted in Schemes 2–4. For the synthesis of the reported multinuclear Pd(II) complexes,³ $[Pd_m(\text{ligand})_n](\text{NO}_3)_{2m}$, **4b**, **5b**, and **6b**, heating a DMSO solution of Pd(II) and the ligand at 90 °C for a few minutes was sufficient to obtain the required assemblies. However, heating Pt(II) and the ligand under the same conditions did not give the related Pt(II) complexes, rather a mixture of products was formed as was evident from the ¹H NMR spectrum of the solution. Increasing the ionic strength by the addition of NaNO₃ increased the lability of the Pt–N bonds and hence self-healing is possible to form a single compound as has been shown in the synthesis of some $[{\text{Pt}}(\text{en})\}_x(\text{ligand})_y](\text{NO}_3)_{2x}$ compounds.⁵

Keywords: Self-assembly; Cage compounds; Platinum; Proton NMR.

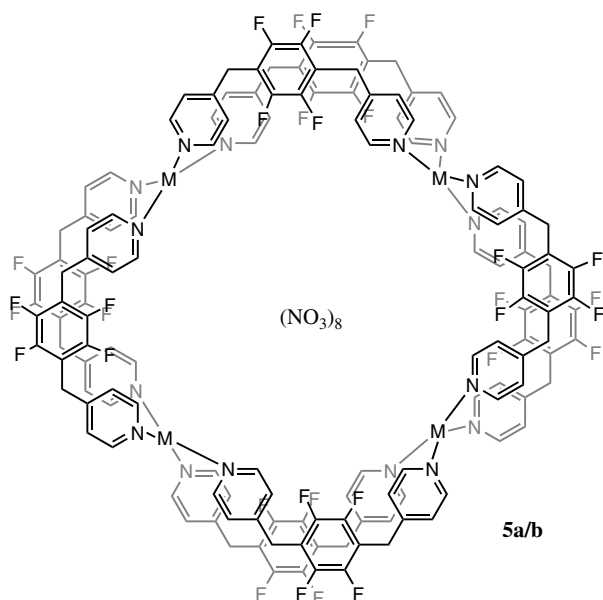
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Scheme 2. The self-assembly obtained from ligand 1. M = Pt: **4a** (this work), M = Pd: **4b** (Ref. 3).



Scheme 4. The self-assembly obtained from ligand 3. M = Pt: **6a** (this work) M = Pd: **6b** (Ref. 3).



Scheme 3. The self-assembly obtained from ligand 2. M = Pt: **5a** (this work) M = Pd: **5b** (Ref. 3).

However, NaNO₃ is not soluble in DMSO thus we used a higher temperature and longer time for the complexation. It was observed that heating the mixture at 120 °C for around 12 h were provided suitable conditions.⁶ The ¹H NMR spectra of the Pt(II) complexes^{6,7} so obtained matched closely with the corresponding spectra of the reported Pd(II) complexes (Fig. 1). The calculated deviation in the positions of the signals was not more than 0.05 ppm. Interestingly, compounds **4a** and **6a** were formed quantitatively. However, in the case of **5a**, although we observed the title compound as the major product some extra signals were also observed in the spectrum. Since the assemblies **4a** and **6a** are formed quantitatively it is logical to assume that the architectures are probably thermodynamically more stable compared to **5a**. The incomplete formation of the required assembly, **5a** could also be due to kinetic problems.

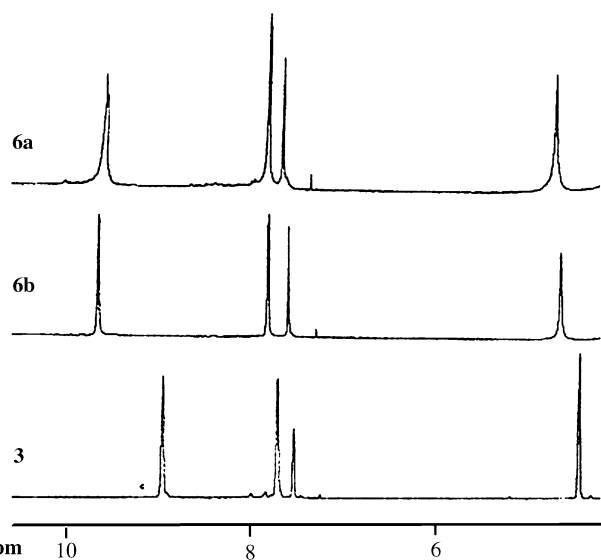
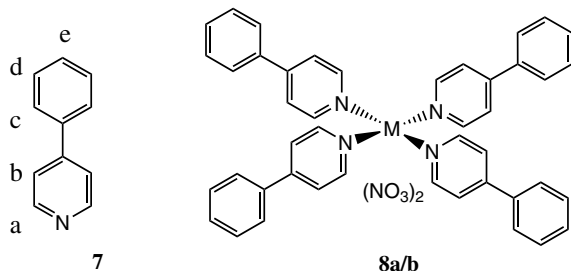


Figure 1. Representative figure showing a comparison of the ¹H NMR spectra of the ligand 3, compound **6a** (this work), and **6b** (Ref. 3) in DMSO-*d*₆.

A point to note here is when the participating metal center, that is, Pd(II) or Pt(II), is not protected then control of all four sites around each metal ion during complexation is required unlike controlling two sites for cis-protected and only one site for triply protected Pt centers. One main principle in metal driven self-assembly is the self-healing of the wrongly formed architectures thus giving rise to thermodynamically favorable compounds. The healing is possible due to the dynamic nature of the metal–ligand bonds. Since the Pt–N bonds are more inert⁸ compared to Pd–N bonds, self-healing is supposed to be comparatively difficult for Pt(II) compounds. Thus it may be difficult to form all four bonds around each Pt(II) in the correct manner. The dynamic nature of



Scheme 5. Ligand **7** and the self-assembly obtained from the ligand. M = Pt: **8a** (this work) M = Pd: **8b** (Ref. 9).

the Pt–N bond could be a result of the polar solvent DMSO and the higher temperature allowing formation of the required $[\{Pt_m(\text{ligand})_n\}(\text{NO}_3)_{2m}]$ assembly.

Complexation of the monodentate ligand 4-phenylpyridine, **7** was performed by combining the ligand with Pt(II) at rt in DMSO to obtain the mononuclear complex $[\text{Pt}(\text{L})_4](\text{NO}_3)_2$, **8a**. The structures of **7** and **8a** are shown in **Scheme 5**. There is only one possible outcome in this case and the complexation was almost complete even at rt indicating the ease of Pt–N bond formation. However, heating the mixture at 120 °C for 1 h provided complete formation of the mononuclear compound. In the case of multinuclear assembly formation the incorrectly formed Pt–N bonds need to be broken and therefore heating is required for a longer time. Thus, the multinuclear Pt(II)-containing cage compounds **4a**, **5a**, and **6a** as detected in solution state could be prepared successfully using the optimized reaction conditions. Once all of the bonds are correctly formed and the Pt(II)-based self-assembly is achieved, the compound must be more robust than the analogous Pd(II) compounds due to the inert nature of Pt–N bonds. What is more important here is the power of the self-assembly route to self-heal the mixture to finally give thermodynamically stable compounds even in the case where inert Pt–N bond breaking and making is required. Remarkably, in compound **6a**, as many as 24 Pt–N bonds are fixed in the correct positions by suitable control of the reaction parameters.

In conclusion, we have prepared a new class of compounds possessing the general formula $[\text{Pt}_m(\text{ligand})_n](\text{NO}_3)_{2m}$.

Acknowledgements

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References and notes

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- Experimental: All the complexes were prepared using the relevant amount of components with a slight excess of the metal using the general procedure outlined here for $[(\text{Pt})_6(\mathbf{3})_8](\text{NO}_3)_{12}$, **6a**. A mixture of PtCl_2 (2.7 mg, 0.01 mmol) and AgNO_3 (3.4 mg, 0.02 mmol) in 1 mL of $\text{DMSO-}d_6$ was heated at 90 °C for 1 h in a centrifuge tube (with screw cap) and the mixture was then centrifuged at rt. To the mixture, ligand **3** (3.5 mg, 0.01 mmol) was added at rt and solubilized by shaking the tube. The mixture was further centrifuged and 0.5 mL of the supernatant was transferred to an NMR sample tube. The NMR tube was heated at 120 °C for 12 h to obtain a solution of the title compound. The complexes were isolated by diffusion of ether/chloroform to the DMSO solutions.
Compound **6a**: ^1H NMR (400 MHz, $\text{DMSO-}d_6$, TMS external): δ 9.61 (d, $J = 5.8$ Hz, 48 H, Py_α), 7.82 (d, $J = 5.3$ Hz, 48H, Py_β), 7.64 (s, 24H, Ar-H), 4.68 (s, 48H, $-\text{CH}_2-$). ^{13}C NMR: (100 MHz, $\text{DMSO-}d_6$, TMS): δ 155.86 (Cq), 151.39 (py_α), 136.96 (Cq), 131.02 (Ar-H), 126.81 (py_β), 41.018–40.017 ($-\text{CH}_2-$ and DMSO). Anal. Calcd for $\text{C}_{192}\text{H}_{168}\text{N}_{36}\text{O}_{36}\text{Pt}_6(\text{dmsO})_{15}$: C, 45.21; H, 4.41; N, 8.55. Found: C, 45.57; H, 4.73; N, 8.20. Mp, decomposed above 295 °C.
- Compound **4a**: ^1H NMR (400 MHz, $\text{DMSO-}d_6$, TMS external): δ 10.10 (d, $J = 4.9$ Hz, 16H, a), 9.23 (s, 8H, c), 9.03–8.99 (m, 16H, b and 4H, g), 8.51 (d, $J = 7.3$ Hz, 8H, d), 8.43 (d, $J = 8.0$ Hz, 8H, f), 8.26 (d, $J = 8.0$ Hz, 8H, h), 8.15 (t, $J = 7.7$ Hz, 8H, e), 8.03 (t, $J = 7.9$ Hz, 4H, i). Refer to **Scheme 1** for numbering system used here. Anal. Calcd for $\text{C}_{112}\text{H}_{80}\text{N}_{12}\text{O}_{12}\text{Pt}_2(\text{dmsO})_5$: C, 57.09; H, 4.32; N, 6.55. Found: C, 57.39; H, 4.05; N, 6.85. Mp, decomposed above 269 °C.
Compound **5a**: ^1H NMR (400 MHz, $\text{DMSO-}d_6$, TMS external): δ 9.75 (d, $J = 5.9$ Hz, 32H, py_α), 8.11 (d, $J = 5.8$ Hz, 32H, py_β), 4.84 and 4.65 (dd, $^2J = 17.3$ Hz, 32H, diastereotopic $-\text{CHH}-$) along with the extra signals mainly at δ 9.50 (d, $J = 5.7$ Hz, py_α) and 8.50 (d, $J = 5.8$ Hz, py_β). Mixture of compounds.
Compound **8a**: ^1H NMR (400 MHz, $\text{DMSO-}d_6$, TMS): δ 9.69 (d, $J = 6.8$ Hz, 8H; a), 8.58 (dd, $J = 5.7$ and 1.3 Hz, 4H; b), 8.37–8.32 (m, 8H; c), 8.04–8.02 (m 12H; d and e). Anal. Calcd for $\text{C}_{44}\text{H}_{36}\text{N}_6\text{O}_6\text{Pt}$: C, 56.23; H, 3.86; N, 8.94. Found: C, 55.91; H, 3.55; N, 8.63. Mp, decomposed above 214 °C.
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