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# Coordination-driven self-assembly in a single pot

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ABSTRACT

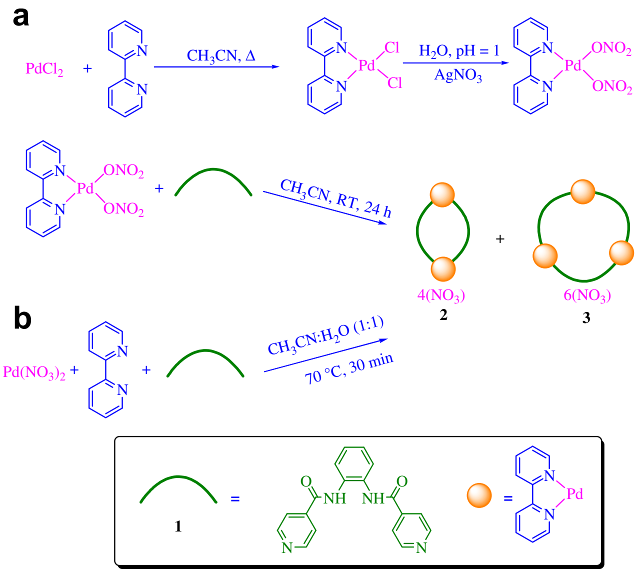
New multinuclear discrete heteroleptic complexes have been synthesized by mixing Pd(II), 2,2′-bipyridine and *N*,*N*′-(1,2-phenylene)diisonicotinamide in a single pot as a new approach. A dimeric molecular rhombus and a trimer in equilibrium are obtained where the dimer is the major product. Similar equilibrium is also observed when classical method is employed for the synthesis. The equilibrium is shifted exclusively in favour of the dimer upon addition of benzene. The complexes are characterized by NMR and ESI-MS methods. Crystal structure of the benzene encapsulated rhombus is presented.

Self-assembly is one of the beautiful aspects of supramolecular chemistry.[1] Based on the nature of self-assembly several metal-assisted multinuclear discrete architectures are reported in the literature.[2] Generally partially protected metal is further complexed with a suitable ligand to get the assembly. The number of accepting sites for the metal centre is lowered by blocking with the protecting units which commonly are chelating in nature. In this work various components consisting of Pd(II), 2,2′-bipyridine (bpy) and *N*,*N*′-(1,2-phenylene) diisonicotinamide are combined in a single pot which results in the formation of exclusive discrete product(s). In comparison with classical method,[2] the one-pot method is less time consuming.

Equimolar mixture of *N*,*N*′-(1,2-phenylene) diisonicotinamide, **1**[3] along with Pd(II) and bpy in $CH_3CN/H_2O$ (1:1) solvent system in a single pot at 70 °C for 30 min gave rise to an equilibrium mixture of binuclear compound **2** as a major product along with a trinuclear complex **3** (Scheme 1b).[4] Concentration variation was studied for the equilibrium of **2** and **3** at 5 and 10 mM of Pd, which gave the ratio as 96:4 and 89:11, respectively. This observation is in accordance with the entropy factor.[5]

The equilibrium mixture was shifted towards **2** by the addition of benzene to this solution (Fig. 1). The upfield shift of **2** in $^1$H NMR suggests that there is a host guest complexation. When the synthesis was attempted by classical method the same equilibrium mixture of **2** and **3** was observed. In this method bpy was added to a hot acetonitrile solution of $PdCl_2$ to prepare $Pd(bpy)Cl_2$ (Scheme 1a).[6] The chloride anion of the isolated $Pd(bpy)Cl_2$ was then exchanged with nitrate by adding $AgNO_3$ in aq $HNO_3$ at pH 1.[6] Thus the formed $Pd(bpy)(NO_3)_2$ upon complexation with ligand **1** at room temperature for 24 h in $CH_3CN$ medium gave rise to the similar equilibrium mixture. The comparison between classical and one-pot method is given in Table 1.

The ESI-MS in water/methanol (1:5) mixture showed peaks corresponding to the loss of four nitrate anions for complex **2** at *m*/*z* 290.42 $[\mathbf{2}-(NO_3)_4]^{4+}$ and loss of six nitrate anions for complex **3** at *m*/*z* 290.84 $[\mathbf{3}-(NO_3)_6]^{6+}$.



**Scheme 1.** Synthesis of **2** and **3** by (a) classical method (b) one-pot method.

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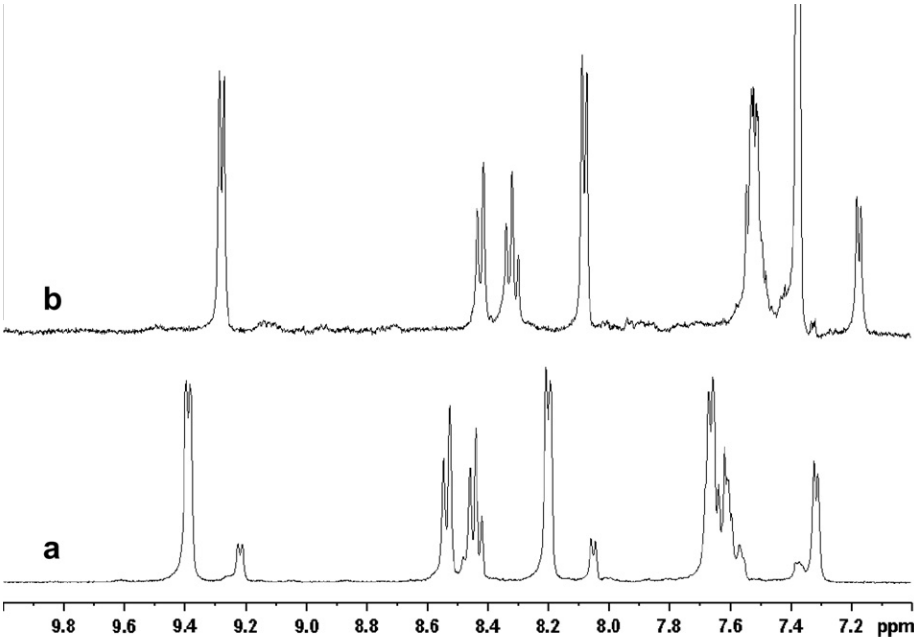


**Figure 1.** $^1$H NMR spectra in $D_2O$ of (a) a mixture of **2** (major) and **3**, (b) benzene $\subset$ **2** emerged from the equilibrium upon addition of benzene.

**Table 1**
Comparison between classical and one-pot method for the synthesis of the mixtures **2** and **3**

| Method | Step | Time (h) | Temperature (°C) | Yield (%) |
|---|---|---|---|---|
| Classical | 1st | 1 | 60 | 92 |
| | 2nd | 0.5 | 60 | 83 |
| | 3rd | 24 | rt | 92[a,b] |
| One pot | one | 0.5 | 70 | 95[b] |

[a] Over all yield is 70%.
[b] similar product ratio of **2** and **3**.

Single crystals were formed within one week by layering benzene to an aqueous solution of the complexes at room temperature. The crystal structure showed a binuclear rhombus structure having a benzene molecule encapsulated in the cavity (Fig. 2).[7] This binuclear complex resembles a rare rhombus architecture where two adjacent arms are occupied by one ligand unit and the square planes of the metal centres are coplanar. The two amide oxygen moieties of a given ligand are almost perpendicular to the square planes of the complexed Pd-centres and point *trans* to amide oxygen of the other ligand unit of the rhombus. Each oxygen form a hydrogen bond (~2.9 Å) intermolecularly with amide NH. Thus one molecule of benzene $\subset$ **2** $\cdot$ $4H_2O$ possesses eight H-bonds by connecting with four neighbouring molecules. The benzene molecule is trapped almost at the centroid of the hydrophobic cavity of this molecular rhombus. Each Pd(II) ion adopts a square planar geometry with Pd–N bond distance of ~2.0 Å and the Pd to Pd distance is ~11.9 Å. The pyridine rings of the ligands are situated orthogonally to the 2,2′-bipyridine ring. The *o*-phenylenediamine moiety of the complexed ligand remains perpendicular to the pyridine rings and slightly out of plane to adjust the geometrical demand of the metal centre. While two nitrates are located the other two are not found.

This method was further established with ligand 1,4-bis(4′-pyridylmethyl)-2,3,5,6-tetrafluorobenzene, **4**. Bidentate non-chelating ligand **4**, $Pd(NO_3)_2$ and bpy at a ratio of 1:1:1 in $CH_3CN/H_2O$ (1:1) gave a single dimeric complex **5** (Scheme 2), which was characterized by $^1$H NMR and ESI-MS.[8,9] The ESI-MS in water/methanol (1:5)

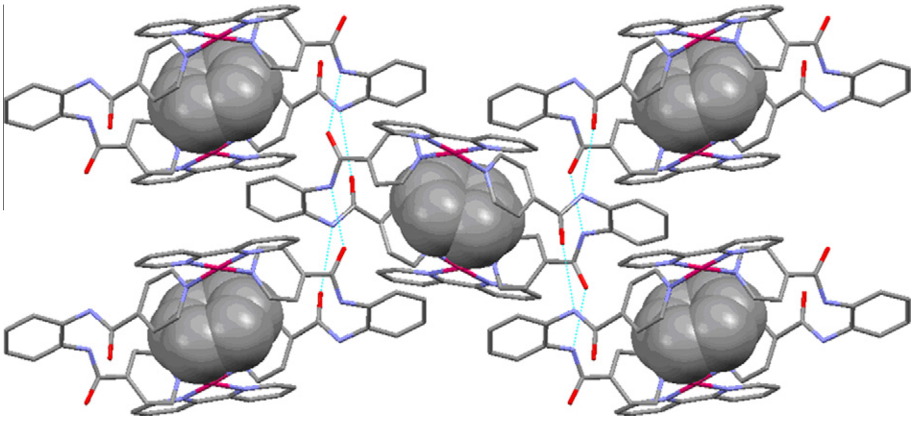
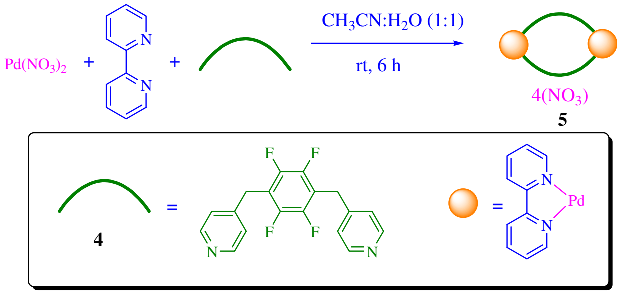


**Figure 2.** Extensive intermolecular hydrogen bonding seen in the crystal structure of benzene $\subset$ **2** $\cdot$ $4H_2O$. Counter anions, hydrogen atoms and water are omitted for clarity. Benzene is shown in space filling style.



**Scheme 2.** Synthesis of complex **5** by one-pot method.

showed a peak corresponding to the loss of four nitrate anions at *m/z* 297.0 [**5**$-(NO_3)_4]^{4+}$.

In conclusion, steric crowding generated by bpy[10] during complexation along with the labile nature of co-ordinate bond between Pd and N was successfully utilized for the preparation of discrete product in a single pot.

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## Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.06.084.

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