

Role of peripheral phenanthroline groups in the self-assembly of self-assembled molecular triangles

MILI C NARANTHATTA, V RAMKUMAR and DILLIP KUMAR CHAND*

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India
e-mail: dillip@iitm.ac.in; dillipiitm@gmail.com

MS received 18 September 2014; accepted 30 September 2014

Abstract. Self-assembled molecular triangles $[\text{Pd}_3(\text{phen})_3(\text{imidazolate})_3](\text{NO}_3)_3$, **1a** and $[\text{Pd}_3(\text{phen})_3(\text{imidazolate})_3](\text{PF}_6)_3$, **1b** are prepared by the combination of imidazole with $\text{Pd}(\text{phen})(\text{NO}_3)_2$ and $\text{Pd}(\text{phen})(\text{PF}_6)_2$, respectively. Imidazole was deprotonated during the complexation reactions and the imidazolate so formed acted as a bis-monodentate bridging ligand to form the bowl-shaped trinuclear architectures of **1a/b**. Relative orientation of the imidazolate moieties can be best described as *syn,anti,anti* as observed in the crystal structure of **1b**. However, in solution state, slow conformational changes are assumed on the basis of ^1H NMR spectral data. The molecular triangles are crafted with three peripheral *phen* units capable of $\pi-\pi$ stacking interactions. Well-fashioned intermolecular $\pi-\pi$ interactions are observed in the solid-state, wherein further self-assembly of already self-assembled triangle is observed.

Keywords. Palladium(II); 1,10-phenanthroline; imidazole; self-assembly; molecular triangle.

1. Introduction

The design and construction of discrete molecular architectures through metal-directed self-assembly have undergone significant development in recent years.¹ These techniques involve self-assembly of multidentate ligands and chosen metal ions to afford infinite or finite self-assembled molecules. The understanding and utilization of all non-covalent interactions including hydrogen bonding² or $\pi-\pi$ stacking³ is of fundamental importance for further development of crystal engineering besides the synthesis of new self-assembled molecules. These weak intermolecular interactions contribute largely to the supramolecular association in the solid state.

The structural advantage of the square-planar coordination environment of palladium(II) has been generally utilized for the construction of molecular architectures by this approach.^{1a-f} Designed discrete structures are known to be achieved from the combination of a variety of palladium(II) components and appropriate ligand. When a *cis*-protected palladium(II) component is treated with suitable bis-monodentate ligand **L**, it provides self-assembly having formula $[\text{Pd}_x(\text{L}')_x(\text{L})_y](\text{monoanion})_{2x}$ where **L'** is the *cis*-protecting unit.^{1a-f} *cis*-Protection has been carried out by using simple bidentate chelating ligands

such as ethylenediamine (*en*), 2,2'-bipyridine (*bpy*), tetramethylethylenediamine (*tmeda*), 1,10-phenanthroline (*phen*), etc.

Although there are reports on several designed palladium(II)-based coordination cage molecules,^{1a-f} various aspects of their chemistry related to crystal engineering are less explored.⁴ We have been investigating the roles of the motifs present in *cis*-protecting units to conceptualize targeted packing of self-assembled coordination compounds in the solid state. We have reported certain binuclear self-assembled coordination cages, designed for pre-defined intermolecular interactions in solid state to direct further self-assembly of the already self-assembled coordination cages.^{4a-b} The $\pi-\pi$ stacking is the targeted intermolecular interactions in our designs. Thus, we have demonstrated a pre-defined packing in the crystal structure of 'opened jaws' type and 'steps type' complexes and considered this kind of packing as 'self-assembly of self-assembly'.^{4a-b} This novel packing behaviour of the already self-assembled molecules are obtained due to the presence of π -surfaces at the strategically located *cis*-protecting moieties located around the palladium(II) centres.

The self-assembly of self-assembly approach has been recently extended by us to trinuclear palladium(II) complexes.⁵ Unfortunately, there are only a limited number of studies on trinuclear complexes having formula $[\text{Pd}_x(\text{L}')_x(\text{L})_y](\text{monoanion})_{2x}$ that are prepared from palladium(II) and bis-monodentate

*For correspondence

ligands.^{1a–f5–7} Further, the trinuclear complexes usually exist in dynamic equilibrium with corresponding bi/tetra-nuclear complexes.⁷ However, there are a few studies where the trinuclear complexes are solely isolated as single discrete products. Despite the above mentioned limitation, we have reported a rare variety of self-assembled molecular triangle $[\text{Pd}_3(\text{bpy})_3(\text{imidazolate})_3](\text{NO}_3)_3$, (figure 1a) having *syn, syn, syn* relative orientation of the bound imidazolate moieties in the solid state.⁵ Further self-assembly of the self-assembled molecular triangle is demonstrated in the solid state, wherein a linear propagation is observed utilizing intermolecular $\pi-\pi$ interactions (figure 1c).⁵ This self-assembly of self-assembly is guided by $\pi-\pi$ stacking interactions due to the presence of a π -surface in the *bpy* units which is the *cis*-protecting moiety around the palladium(II) centers.

We have prepared a modified version of the above mentioned trinuclear complex by incorporating *phen*

units as *cis*-protecting moiety around the palladium(II) centers instead of *bpy* (scheme 1). The modification was undertaken so as to explore the consequence of the presence of extended π -surfaces on the crystal packing. It was anticipated that the judicious introduction of extended π -surfaces in *cis*-protecting units at the corners of a triangular architecture should give rise to specific packing via $\pi-\pi$ stacking interactions. Interestingly, relative orientation of the bound imidazolate moieties in the studied complex in the solid state is found to be *syn, anti, anti*. During this study, we observed linear chain-like arrangement of the molecules by using all the three *phen* units as shown in figure 1d. This observation is in contrast to the linear arrangement of triangular panels where only two out of the three *bpy* units are used in a given chain. This observation demonstrates the influence and importance of subtle change in π -surface on the crystal engineering aspects of the molecular triangles.

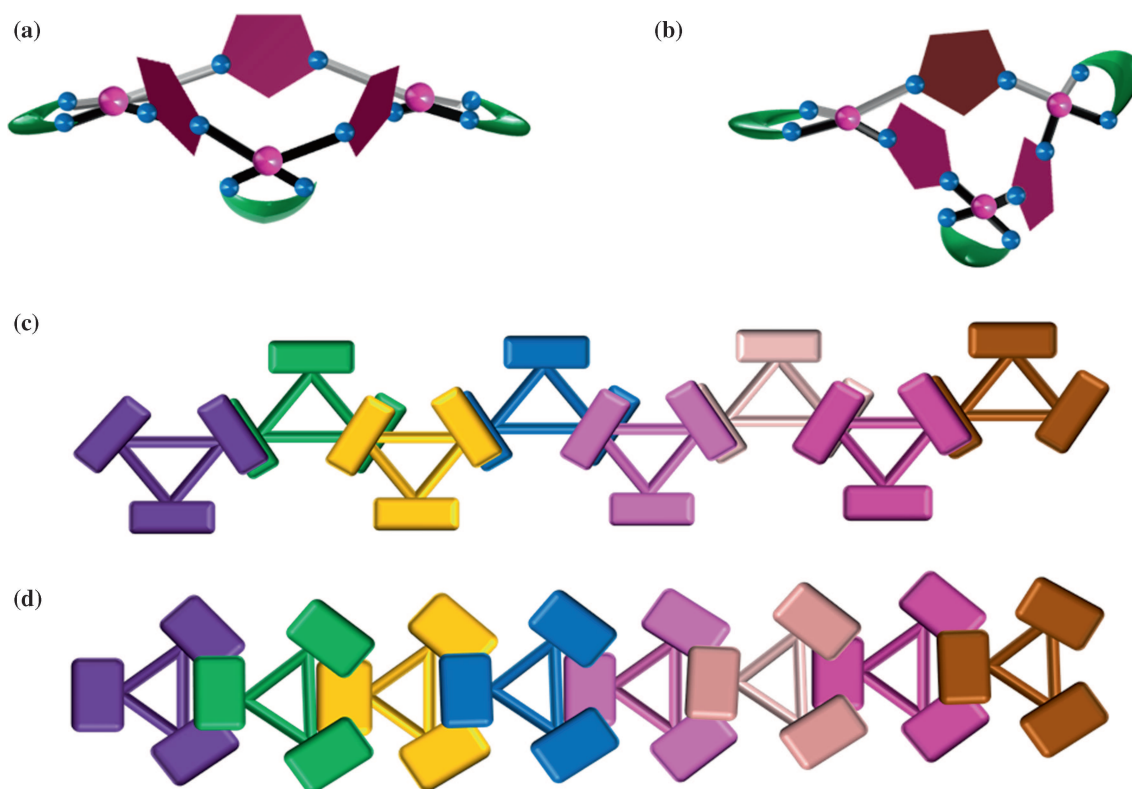


Figure 1. Cartoon diagram showing the relative orientation of the bound imidazolate units in the trinuclear complexes (a) *syn, syn, syn*-form in $[\text{Pd}_3(\text{bpy})_3(\text{imidazolate})_3](\text{NO}_3)_3$ (reference 5); and (b) *syn, anti, anti*-form in $[\text{Pd}_3(\text{phen})_3(\text{imidazolate})_3](\text{NO}_3/\text{PF}_6)_3$, **1a/b**. Cartoon diagram of self-assembly of self-assembled molecular triangles using $\pi-\pi$ stacking interactions in (c) $[\text{Pd}_3(\text{bpy})_3(\text{imidazolate})_3](\text{NO}_3)_3$ (reference 5); and (d) $[\text{Pd}_3(\text{phen})_3(\text{imidazolate})_3](\text{PF}_6)_3$, **1b**. (Each triangular unit in (c)/(d) represents the core of the trinuclear molecules.)

2. Experimental

2.1 Materials

PdCl_2 was obtained from Aldrich, whereas AgNO_3 , AgPF_6 , imidazole (**L·H**) and all the common solvents were obtained from Spectrochem, India. The deuterated solvent ($\text{DMSO-}d_6$) was obtained from Aldrich and Cambridge Isotope Laboratories. ^1H and all NMR spectral data were obtained from a Bruker 500 MHz FTNMR spectrometer using external Tetramethylsilane (TMS) in CDCl_3 as reference. The mass spectra were obtained from a Micromass Q-TOF Mass Spectrometer. The crystal structure was determined using a Bruker X8 Kappa XRD instrument. The *cis*-protected palladium(II) component was obtained following well-known processes.⁸ Imidazole was used as such for complexation without any purification.

2.2 Synthesis of $[\text{Pd}_3(\text{phen})_3(\text{imidazolate})_3](\text{NO}_3)_3$, **1a**

To a solution of $\text{Pd}(\text{phen})(\text{NO}_3)_2$ (11.0 mg, 0.028 mmol) in 1:1 acetonitrile–water (2.8 mL), imidazole, **L·H** (1.93 mg, 0.028 mmol) was added and the mixture was stirred at room temperature for 2 h. The resulting solution was evaporated by standing at room temperature and dried under vacuum to afford a white solid as the product. Yield: (90%). M.P.: 230°C. ^1H NMR (δ 500 MHz, $\text{DMSO-}d_6$, external CDCl_3/TMS): 9.68 (d, $J = 10.5$ Hz, 2H, H_c), 9.1 (d, $J = 6$ Hz, 2H, H_a), 8.98 (s, 2H, H_d), 8.72–8.69 (m, 2H, H_b), 8.1–7.5 (broad signals, 2H, H_f); ESI–MS: $m/z = 353$ corresponding to $[\mathbf{1}-3\text{NO}_3]^{3+}$ and 560 corresponding to $[\mathbf{1}-2\text{NO}_3]^{2+}$.

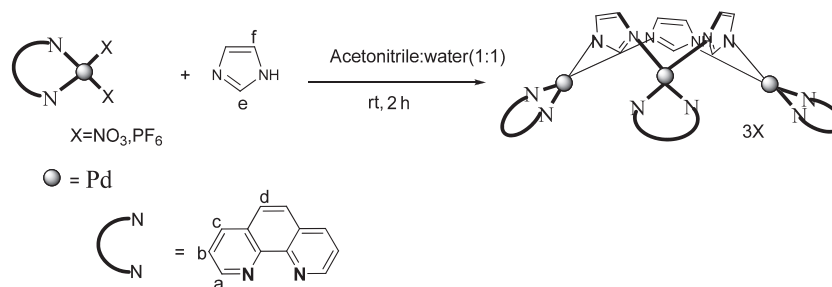
2.3 Synthesis of $[\text{Pd}_3(\text{phen})_3(\text{imidazolate})_3](\text{PF}_6)_3$, **1b**

To a solution of $\text{Pd}(\text{phen})\text{Cl}_2$ (11 mg, 0.03 mmol) in 1:1 acetonitrile–water (3 mL), silver hexafluorophosphate

was added (15.5 mg, 0.06 mmol), which led to immediate precipitation of AgCl . The resulting mixture was heated for 30 min and centrifuged. The yellow colour solution of $\text{Pd}(\text{phen})(\text{PF}_6)_2$ so formed was separated by filtration. To the clear yellow solution, ligand **L·H** (2 mg, 0.03 mmol) was added and the mixture was stirred at room temperature for about 2 h. The resulting solution was evaporated by standing at room temperature and dried under vacuum to afford a yellow solid as the product. Yield: (90%) M.P.: 120°C (decomposed). ^1H NMR (δ 500 MHz, $\text{DMSO-}d_6$, external CDCl_3/TMS): 9.67 (d, $J = 9$ Hz, 2H, H_c), 9.1 (d, $J = 6.5$ Hz, 2H, H_a), 8.97 (s, 2H, H_d), 8.72–8.70 (m, 2H, H_b), 8.13–7.93 (broad signals, 2H, H_f); ESI–MS: $m/z = 353$ corresponding to $[\mathbf{1b}-3\text{PF}_6]^{3+}$ and 601 corresponding to $[\mathbf{1b}-2\text{PF}_6]^{2+}$. Single crystals of **1b** were obtained by slow diffusion of carbon tetrachloride into solution of **1b** in acetonitrile–water.

2.4 Single crystal X-ray diffraction

X-ray data were collected with a Bruker AXS Kappa Apex II CCD diffractometer equipped with graphite monochromated $\text{Mo}(\text{K}\alpha)$ ($\lambda = 0.7107\text{\AA}$) radiation. Crystal fixed at the tip of the glass fibre was mounted on the goniometer head and was optically centered. The automatic cell determination routine, with 32 frames at three different orientations of the detector was employed to collect reflections and the program APEX2-SAINT (Bruker 2004) was used to find the unit cell parameters. Four-fold redundancy per reflection was utilized for achieving good absorption correction using a multiscan procedure. Besides absorption, Lorentz polarization and decay correction were applied during data reduction. The program SADABS was used for absorption correction using the multiscan procedure. The structures were solved by direct methods using SHELXL 2013 (Sheldrick 2013)⁹ and refined by full-matrix least-squares techniques using SIR92 (WinGIX) computer program. All hydrogen



Scheme 1. Synthesis of the self-assembled trinuclear complexes $[\text{Pd}(\text{phen})_3(\text{imidazolate})_3](\text{X})_3$, **1a/b** ($\text{X} = \text{NO}_3$, **1a**; PF_6 , **1b**).

atoms were fixed at chemically meaningful positions and riding model refinement was applied. Molecular graphics were generated using Mercury programs. The crystal data with refinement details are summarized in table 1.

3. Results and Discussion

Imidazolate is a bent bis-monodentate bridging ligand which upon complexation with right-angled *cis*-protected palladium(II) component, i.e., Pd(phen)(NO₃)₂, should yield a cyclic bowl type cage with spontaneous deprotonation of imidazole (**L·H**). Pyrazolate or substituted imidazolate bridged complexes are reported with this type of deprotonation processes.^{6a,b,10} Imidazole groups can be orientated either in a *syn, syn, syn* (cone conformer)^{6a-c} or *syn, anti, anti* (alternate conformer)¹¹ fashion in the cages. Based on this idea, we have recently reported a bowl-shaped trinuclear molecule, [Pd₃(bpy)₃(imidazolate)₃](NO₃)₃ and investigated the possible intermolecular interactions among such bowls in which the π -surface containing *cis*-protecting unit such as *bpy* was crafted around the palladium(II).⁵ In order to compare the influence of the π -surface area

located at the strategic position on the crystal packing, the *cis*-protecting unit with extended π -surface such as *phen* was considered to craft around the palladium(II). Phenanthroline units have extended aromatic ring system which could possibly make a difference in the π – π stacking when compared to *bpy* units.³ The reaction of *cis*-Pd(phen)(X)₂ with one equivalent of imidazole, **L·H** in acetonitrile: water (1:1) at room temperature over a period of 2 h lead to the formation of [Pd(phen)₃(imidazolate)₃](X)₃, **1a/b** (scheme 1). A fascinating intermolecular association in the solid state was observed for [Pd(phen)₃(imidazolate)₃](PF₆)₃, **1b** as shown in figure 1d and discussed in a later section. We observed the trinuclear cages with *syn, anti, anti*-form (alternate conformer). To the best of our understanding, this is a rare example where a imidazolate-bridged trinuclear palladium(II) complex is isolated in *syn, anti, anti*-conformation. However, a benzimidazolate-bridged trinuclear platinum(II) complex with *syn, anti, anti*-conformation is known.¹¹ Analysis of the crystal structures of cages **1b** shows π – π stacking interactions between planar *phen* units as anticipated. The complex **1b** displays the packing where triangular molecules are arranged in a linear sequence via π – π stacking interactions as shown in figure 1d. A detailed description of the synthesis of the complexes and crystal structures is discussed below.

Table 1. Crystallographic data and structure refinement parameters of **1b** (CCDC No 990213).

| Empirical formula | C ₄₇ H ₃₆ F ₁₈ N ₁₃ P ₃ Pd ₃ |
|---|--|
| Formula weight | 1537.00 |
| Crystal system | Orthorhombic |
| Space group | P n m a |
| <i>a</i> (Å) | 27.4761(5) |
| <i>b</i> (Å) | 22.2198(4) |
| <i>c</i> (Å) | 8.8846(2) |
| α (°) | 90 |
| β (°) | 90 |
| γ (°) | 90 |
| Volume (Å ³) | 5424.17(18) |
| <i>Z</i> | 4 |
| Wavelength (Å) | 0.71073 |
| Temperature (K) | 296(2) |
| Calculated density (g/cm ³) | 1.882 |
| Absorption coefficient (mm ^{−1}) | 1.184 |
| <i>F</i> (000) | 3016 |
| Crystal dimensions (mm) ³ | 0.380×0.150×0.100 |
| θ min/max (deg) | 1.74/24.99 |
| Reflections collected/unique | 68547/4923 [R(int) = 0.0416] |
| Data/restraints/parameters | 4923/0/392 |
| Goodness-of-fit on <i>F</i> ² | 1.052 |
| Final <i>R</i> indices [I > 2σ(I)] | R1 = 0.0395, wR2 = 0.1039 |
| <i>R</i> indices (all data) | R1 = 0.0511, wR2 = 0.1140 |
| Largest difference peak and hole (Å ^{−3}) | 1.067 and −0.784 |

3.1 Synthesis and characterization of the M₃L'₃L₃ self-assembly

The complexes **1a/b** are prepared by the combination of equimolar quantities of the ligand **L·H** and *cis*-Pd(phen)(X)₂ in acetonitrile–water (1:1) at room temperature (scheme 1). Trinuclear complexes of formula [Pd(phen)₃(imidazolate)₃](X)₃, were isolated in a quantitative manner. The trinuclear complexes are characterized by ¹H NMR, H–H COSY and electrospray ionization mass spectrometry (ESI–MS) (see supporting information). Molecular structure of the complex **1b** was also confirmed by single crystal XRD method. The ¹H NMR spectra of the complex **1a** (figure 2) and **1b** have been recorded in DMSO-*d*₆. The signals of the protons present in the *phen* units are observed at expected positions. The imidazolate protons designated as H_f appeared as broad signals spanning a range of 0.62 ppm. However, the protons designated as H_e are probably merged inside the other signals. The NMR data indicate a slow conformational movement in the solution state due to the possibility of formation of *syn, syn, syn* and *syn, anti, anti* conformers and other intermediates. The same behaviour was observed in solution

state for the recently reported bowl-shaped complex $[\text{Pd}_3(\text{bpy})_3(\text{imidazolate})_3](\text{NO}_3)_3$; which clearly shows that it occurs due to the peculiarity of imidazole rings to flip into different conformers in solution state.⁵ Formation of the trinuclear complex in the solution state was confirmed from ESI-MS data of the complex. The mass spectrum of **1a** shows peaks at $m/z = 353$ and 560 corresponding to $[\mathbf{1a} - 3\text{NO}_3]^{3+}$ and $[\mathbf{1a} - 2\text{NO}_3]^{2+}$, respectively. The mass spectrum of **1b** shows peaks at $m/z = 353$ and 601 corresponding to $[\mathbf{1b} - 3\text{PF}_6]^{3+}$ and $[\mathbf{1b} - 2\text{PF}_6]^{2+}$, respectively.

3.2 Crystal structure of $[\text{Pd}_3(\text{phen})_3(\text{L})_3](\text{PF}_6)_3$, **1b**

Single crystals suitable for X-ray analysis were obtained by slow diffusion of carbon tetrachloride into solution of **1b** in acetonitrile–water. The complex crystallized in orthorhombic space group Pnma . The structure contains $[\text{Pd}(\text{phen})_3(\text{imidazolate})_3]^{3+}$ cations, three hexafluorophosphate ions and one acetonitrile molecule. Two different views of the crystal structures of the complexed cation are shown in figure 3. Coordination geometry around the metal centres and the related bond lengths and bond angles in the structure

are found to be in the expected range. The bound imidazolate units are orientated in *syn*, *anti*, *anti* manner in the complexed cation of **1b**. Analysis of the crystal structure revealed several intermolecular interactions. Apparently, the π -surface of the *cis*-protecting group along with the relative conformation of the bound imidazolate groups controlled the intermolecular interactions, which is discussed in the next section. The crystallographic parameters of **1b** are listed in table 1.

The imaginary plane created by the three palladium(II) centres in the complex is considered as the reference plane of the molecular triangle. The three Pd atoms form an almost equilateral triangle with Pd–Pd non-bonded distances of 5.95, 5.95 and 6.01 Å. The dihedral angles between bound imidazolate **L** and the triangular-Pd plane are 70.60, 70.60 and 73.95°. The dihedral angles between ‘*phen*’ plane and the reference plane are 16.28, 16.28 and 17.05°. The C2 carbon of the one of the bound imidazolate moieties is pointed opposite to the C2 carbons of the other two bound imidazolate moieties. Thus, the overall geometry deviates from our previously reported bowl-shaped molecule having *bpy* units as *cis*-protecting agent.

The packing of the molecular triangles in the crystal structure of **1b** is shown in figure 4. Two selected

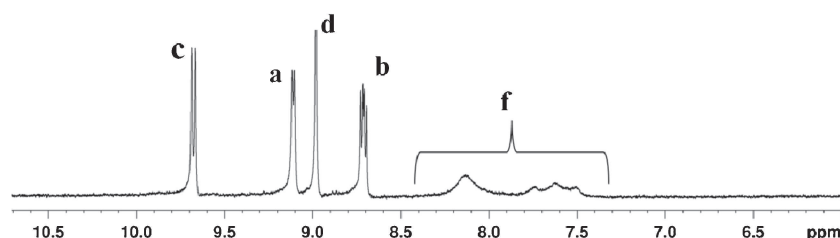


Figure 2. 500 MHz ^1H NMR spectrum in $\text{DMSO}-d_6$ (TMS as external standard) for $[\text{Pd}_3(\text{phen})_3(\text{imidazolate})_3](\text{NO}_3)_3$, **1a** (see supplementary information for the ^1H NMR of **1b**).

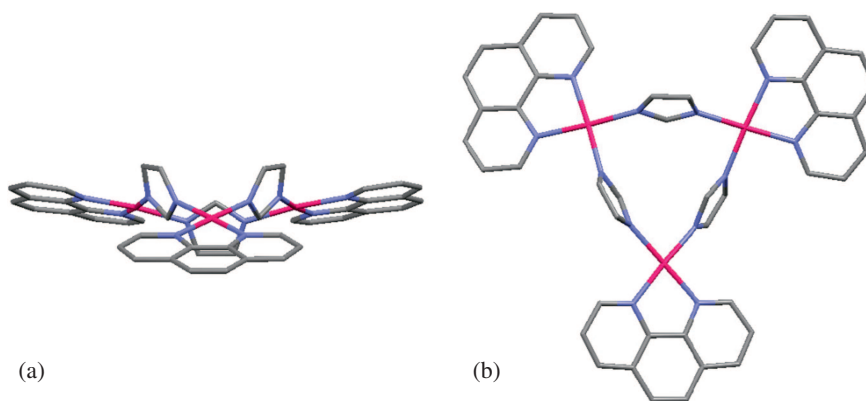


Figure 3. Crystal structure of the trinuclear complex **1b**. Views along the axis: (a) parallel and (b) perpendicular to the imaginary triangle created by joining the three metal centres.

portions from the packing are also shown in figures 5 and 6 for a better description. Adjacent molecules in the packing are associated with each other by intermolecular $\pi-\pi$ stacking interactions where one triangular unit of **1b** is stacked with four other molecules. A given molecule interacts with two molecules along a -axes and two other molecules along a direction somewhat diagonal between the b - and c -axes. As shown in figure 5, along the a -axis, face-to-face overlap of the *phen* units

is observed in a linear manner where one *phen* unit of a triangle overlaps two *phen* units of the adjacent triangle. In a linear chain, each molecular triangle possesses interaction with two other triangles. The linear chains are stacked along the c -axis; however, they are separated by the solvent molecules, that is, acetonitrile. Figure 6 depicts the packing along a direction somewhat diagonal to the b - and c -axes. Both edge-to-face and face-to-face overlaps are seen in this direction.

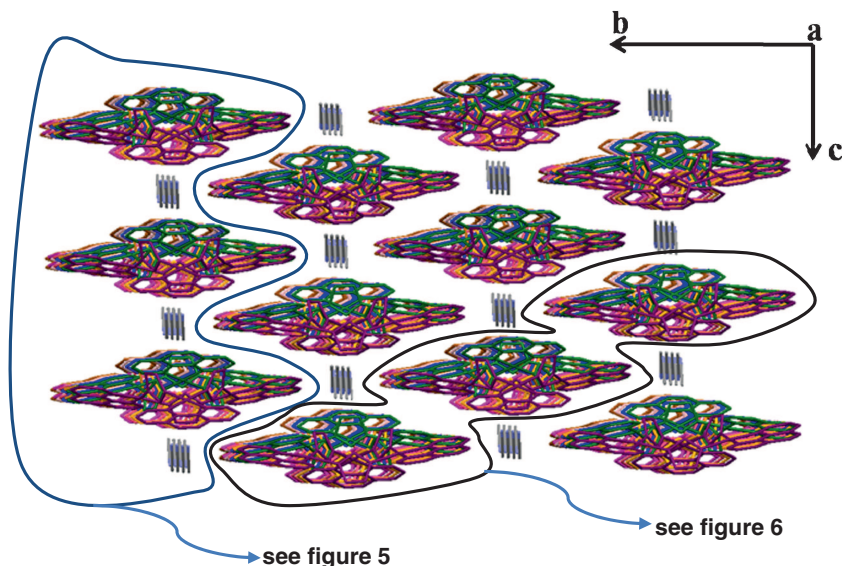


Figure 4. Packing of the molecules in the crystal structure of **1b**, in capped stick model (hydrogen atom and anions are not shown).

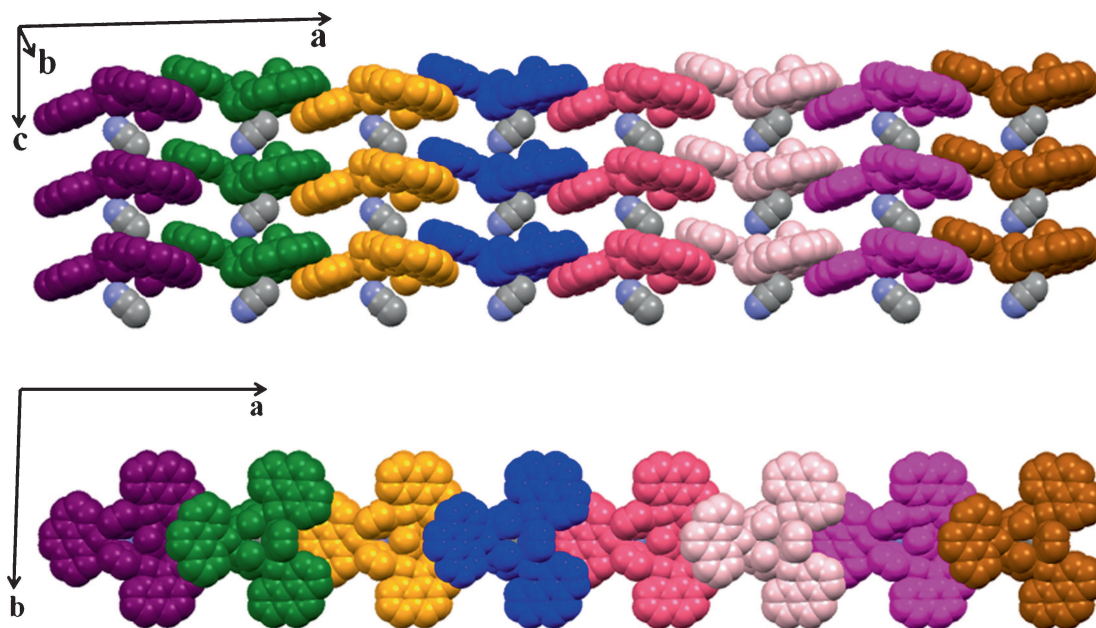


Figure 5. Packing of the molecules in the crystal structure of **1b**, in spacefill model. One of the encircled portions of figure 4 is shown in two different orientations.

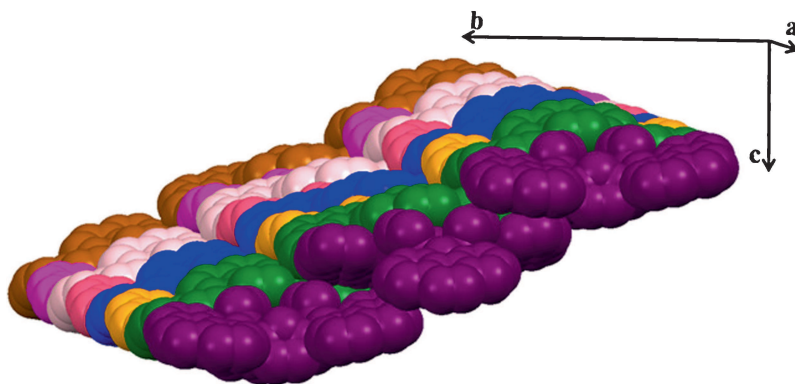


Figure 6. Packing of the molecules in the crystal structure of **1b**, one of the encircled portions of figure 4.

4. Conclusion

Molecular triangles are prepared using *cis* protected palladium(II) components as the metal fragments and imidazole as the ligand. Relative orientation of the bound imidazolate units is observed in the rare *syn*, *anti*, *anti*-form of a triangle in the solid state. The presence of the extended π -surface in the *cis*-protecting group, that is, the *phen* units displayed significant influence on the packing of palladium(II)-based self-assemblies in the solid state as demonstrated and compared with analogues molecule with *bpy* as the *cis*-protecting agent.

Supplementary Information

The ^1H NMR, H-H COSY, ESI-MS spectra are provided (figures S1–S9). X-ray crystallographic data in CIF format for the structure of **1b** are also included. For details, see www.ias.ac.in/chemsci.

Acknowledgements

We thank DST, India (Project No. SB/S1/IC-05/2014) for financial support. We acknowledge the single crystal X-ray Diffractometer facility funded by IIT Madras.

References

- (a) Yoshizawa M and Klosterman J K 2014 *Chem. Soc. Rev.* **43** 1885; (b) Han M, Engelhard D M and Clever G H 2014 *Chem. Soc. Rev.* **43** 1848; (c) Cook T R, Zheng Y-R and Stang P J 2013 *Chem. Rev.* **113** 734; (d) Debata N B, Tripathy D and Chand D K 2012 *Coord. Chem. Rev.* **256** 1831; (e) Fujita M, Tominaga M, Hori A and Therrien B 2005 *Acc. Chem. Res.* **38** 371; (f) Northrop B H, Zheng Y-R, Chi K-W and Stang P J 2009 *Acc. Chem. Res.* **42** 1554; (g) Smulders M M J, Riddell I A, Browne C and Nitschke J R 2013 *Chem. Soc. Rev.* **42** 1728; (h) Thanasekaran P, Lee C-H and Lu K-L 2014 *Coord. Chem. Rev.* **280** 96; (i) Teo P and Hor A T S 2011 *Coord. Chem. Rev.* **255** 273
- (a) Desiraju G R 2000 *J. Chem. Soc., Dalton Trans.* 3745; (b) Desiraju G R 2011 *Cryst. Growth Des.* **11** 896; (c) Beatty A M 2003 *Coord. Chem. Rev.* **246** 131
- Janiak C 2000 *J. Chem. Soc., Dalton Trans.* 3885
- (a) Naranthatta M C, Das D, Tripathy D, Sahoo H S, Ramkumar V and Chand D K 2012 *Cryst. Growth Des.* **12** 6012; (b) Tripathy D, Ramkumar V and Chand D K 2013 *Cryst. Growth Des.* **13** 3763; (c) Krishna Kumar D, Das Amitava and Dastidar P 2006 *Cryst. Growth Des.* **6** 216; (d) Navarro J A R, Romero M A and Salas J M 1997 *J. Chem. Soc., Dalton Trans.* 1001
- Naranthatta M C, Ramkumar V and Chand D K 2014 *J. Chem. Sci.* **126** 1493
- (a) Liu L-X, Huang H-P, Li X, Sun Q-F, Sun C-R, Li Y-Z and Yu S-Y 2008 *Dalton Trans.* 1544; (b) Ning G-H, Xie T-Z, Pan Y-J, Li Y-Z, Yu S-Y 2010 *Dalton Trans.* 39 3203; (c) Yu S-Y, Huang H, Liu H-B, Chen Z-N, Zhang R and Fujita M 2003 *Angew. Chem., Int. Ed.* **42** 686; (d) Tzeng B-C, Kuo J-H, Lee Y-C and Lee G-H 2008 *Inorg. Chim. Acta* **361** 2515; (e) Qin Z, Jennings M C and Puddephatt R J 2001 *Chem. Commun.* 2676; (f) Ghosh S, Turner D R, Batten S R and Mukherjee P S, 2007 *Dalton Trans.* 1869; (g) Li S-H, Huang H-P, Yu S-Y, Li Y-Z, Huang H, Sei Y and Yamaguchi K 2005 *Dalton Trans.* 2346; (h) Qin Z, Jennings M C and Puddephatt R J 2002 *Inorg. Chem.* **41** 3967; (i) Teo P, Koh L L, Hor T S A 2008 *Inorg. Chem.* **47** 6464; (j) Bar A K, Chakrabarty R, Chi K-W, Batten S R and Mukherjee P S 2009 *Dalton Trans.* 3222; (k) Steffen A, Braun T, Neumann B and Stammler H-G 2007 *Angew. Chem., Int. Ed.* **46** 8674
- (a) Fujita M, Sasaki O, Mitsuhashi T, Fujita T, Yazaki J, Yamaguchi K and Ogura K 1996 *Chem. Commun.* 1535; (b) Diaz P, Tovilla J A, Ballester P, Benet-Buchholz J and Vilar R 2007 *Dalton Trans.* 3516. (c) Ghosh S and Mukherjee P S 2009 *Inorg. Chem.* **48** 2605. (d) Ma G, Jung YS, Chung D S and Hong J-I 1999 *Tetrahedron Lett.* **40** 531; (e) Ferrer M, Gutierrez A, Mounir M, Rossell O, Ruiz E, Rang A and Engeser M 2007 *Inorg. Chem.* **46** 3395
- (a) Wimmer S and Castan P 1989 *J. Chem. Soc., Dalton Trans.* 403; (b) Drew H D K, Pinkard, F W, Preston G H and Wardlaw W 1932 *J. Chem. Soc.* 1895
- Sheldrick G M 2013 *SHELXL 2013*, University of Göttingen, Germany

10. (a) Yu S-Y, Jiao Q, Li S-H, Huang H-P, Li Y-Z, Pan Y-J, Sei Y and Yamaguchi K 2007 *Org. Lett.* **9** 1379; (b) Yu S-Y, Huang H-P, Li S-H, Jiao Q, Li Y-Z, Wu B, Sei Y, Yamaguchi K, Pan Y-J and Ma H-W *Inorg. Chem.* 2005 **44** 9471; (c) Steffen A, Braun T, Neumann B and Stammer H-G 2007 *Angew. Chem., Int. Ed.* **119** 8828
11. Lai S-W, Chan M C-W, Peng S-M and Che C-M 1999 *Angew. Chem., Int. Ed.* **38** 669