Inorganica Chimica Acta 372 (2011) 71–78

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

A model study of alternative approach toward a class of palladium(II) based self-assembly

Niladri Bihari Debata, V. Ramkumar, Dillip Kumar Chand *

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, Tamil Nadu, India

ARTICLE INFO

Article history:
Available online 2 March 2011

Dedicated to Prof. S.S. Krishnamurthy.

Keywords:
Palladium
Self-assembly
Non-covalent interactions
One pot synthesis

ABSTRACT

A different approach developed for the preparation of palladium(II) based complexes $[(Pd(bpy))_x(L)_y](NO_3)_{2x}$ is modelled by using 4-phenylpyridine as ligand (**L** = **1**). Various solvent systems are inspected to optimize the reaction condition for the preparation of the model complex $[Pd(bpy)(4\text{-phenylpyridine})_2](NO_3)_2$. The model complex is obtained quantitatively as a single product from a 1:1:2 mixture of $Pd(NO_3)_2$, 2,2′-bipyridine and 4-phenylpyridine when stirred at room temperature in CH_3CN:H_2O (1:1). The same reaction is performed in CD_3CN:D_2O (1:1) to monitor the progress of the reaction by recording ^1H NMR. The kinetic products that formed initially got self-healed to give the desired product with in 6 h. However, in DMSO-d_6 spontaneous arrangement leading to the targeted complex was observed and no kinetic product could be detected. When a similar reaction is performed with ethylenediamine instead of 2,2′-bipyridine a mixture of compounds are observed. Theoretical calculation throws some light on the principle behind the success of this method for the bpy based systems. The assembly, $[Pd(bpy)(4\text{-phenylpyridine})_2](NO_3)_2$ has been characterised by NMR, ESI-MS and single-crystal X-ray diffraction methods.

1. Introduction

Synthesis of coordination cage molecules by metal mediated self-assembly routes has received enormous attention during the last two decades [1]. The number of metal centres in these resulting assemblies is mainly attributed to the disposition and number of binding sites in the ligand as well as preferred coordination geometry of the metal. Among the metal centres being employed, the diamagnetic palladium(II) deserves a unique place due to its almost rigid square planar coordination geometry and moderately labile metal–ligand interactions usually resulting in thermodynamically controlled discrete products. A variety of molecular architectures including 3-dimensional cavities are constructed by using either Pd(II) salts [2] or partially protected Pd(II) components [3] and suitable ligands. The number of accepting sites around the metal centre is lowered by blocking them with protecting units which commonly are bidentate and chelating in nature. Partially protected Pd(II) components such as *cis*-Pd(X–X)(monoanion)$_2$ are usually complexed with chosen ligands to get the desired assemblies. However, in some cases mixture of two or more discrete products are also possible whose ratio can be modulated by optimizing parameters like concentration, solvent or guest molecules [4]. Classical method for the complexation of a separately prepared sample of $Pd(bpy)(NO_3)_2$ with a suitable ligand **L** is known to result the discrete assembly $[\{Pd(bpy)\}_x(\mathbf{L})_y](NO_3)_{2x}$ [5].

A new method for the synthesis of $[\{Pd(bpy)\}_x(\mathbf{L})_y](NO_3)_{2x}$ is reported by us [6] where the cage molecules could be prepared in a single step in one pot by combining bpy, $Pd(NO_3)_2$ and a bidentate ligand in contrast to the multistep classical synthesis. The method was validated by using two different bidentate ligands where the products formed by classical and one pot method are identical. In the present work we have tracked the progress of one pot synthesis of the mononuclear model complex [7] $[Pd(bpy)(4\text{-phenylpyridine})_2](NO_3)_2$ in order to comprehend the rationale behind the success of the one pot synthesis.

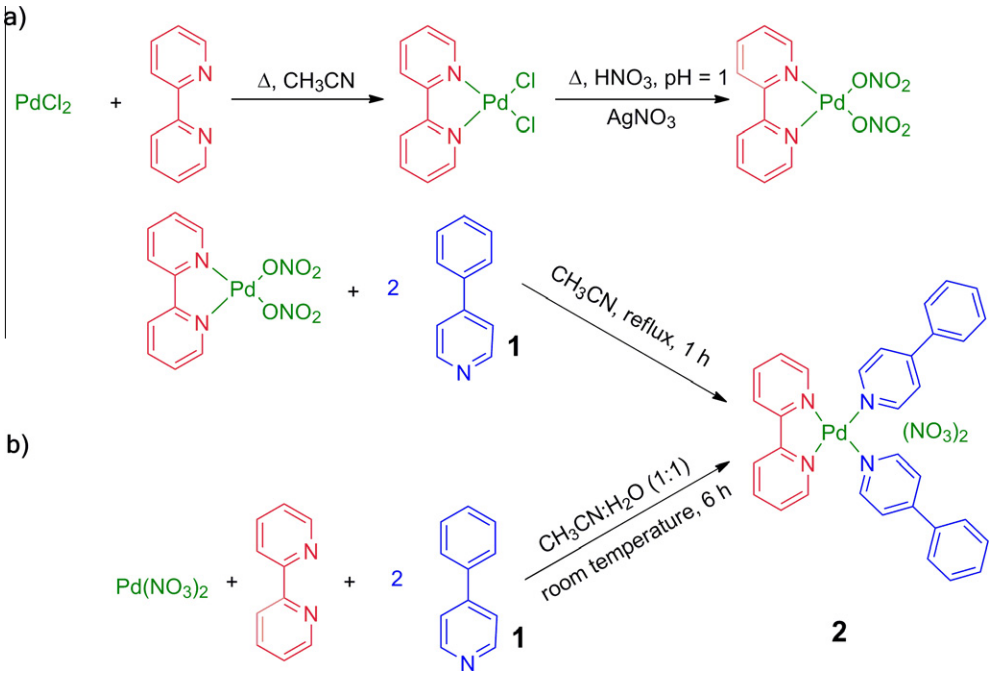
2. Results and discussion

2.1. One pot synthesis of the model complex $[Pd(bpy)(4\text{-phenylpyridine})_2](NO_3)_2$, 2: feasible

A mixture of $Pd(NO_3)_2$, bpy and ligand **1** at a ratio of 1:1:2 was taken in CH_3CN:H_2O (1:1) medium and stirred overnight at room temperature followed by evaporation of the solvents also at room temperature using high vacuum. The isolated solid showed the formation of **2** as a single compound (Scheme 1b) whose identity was confirmed by comparing the ^1H NMR and ESI-MS spectra of the sample prepared by classical method (Scheme 1a) [7]. In comparison with one pot synthesis, the classical method of preparation of **2** is a time consuming and multi-step process. In the classical

* Corresponding author. Fax: +91 44 2257 4202.
E-mail address: dillip@iitm.ac.in (D.K. Chand).

0020-1693/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2011.02.009



Scheme 1. Synthesis of **2** by (a) classical method (Refs. [7] and [8]); (b) one pot synthesis (this work).

method bpy was added to a hot acetonitrile solution of $PdCl_2$ to prepare $Pd(bpy)Cl_2$ which is also commercially available (Scheme 1a) [8]. 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. Thus formed $Pd(bpy)(NO_3)_2$ upon complexation with ligand **1** gave rise to **2**. The mass spectrum of **2** prepared by either method showed identical peaks at *m/z* 286.1 corresponding to $[\mathbf{2}-2(NO_3)]^{2+}$ formed due to the loss of two nitrate anions. Single crystal of **2** further supported the formation of the compound. Comparison between classical and one pot method for the synthesis of **2** is given in Table 1.

Other solvent systems were tried to check the feasibility of the reaction. In CH_3OH reduction of Pd(II) was observed [9] where as in CH_3CN medium, precipitation of **4** (Fig. 1) was observed thus hindering the progress of the reaction. When this reaction was tried in H_2O some amount of brown precipitate was observed. The aqueous supernatant was found to contain majority of **4** along with **2** and some other unidentified products. In case of CH_3OH:H_2O (1:1) as the medium, reduction of Pd(II) was again observed. This suggests the superiority of CH_3CN:H_2O as the best system for one pot synthesis.

The complexation reaction was further conducted in CD_3CN:D_2O mixture (1:1) so as to monitor the progress of the reaction by recording ^1H NMR spectra at different time interval. Initially **3**, **4** and some other complexes were observed as kinetic products along with the desired complex **2** (Figs. 1 and 2). Formation of **3** and **4** was confirmed by comparing the ^1H NMR spectra of the pure compounds recorded in CD_3CN:D_2O mixture (1:1). Within 6 h at room temperature all kinetic products disappeared making the complex **2** as a single product. ESI-MS for this reaction mixture was recorded within 15 min of mixing which showed peaks at *m/z* = 286.05 $[\mathbf{2}-2(NO_3)]^{2+}$, 363.12 $[\mathbf{3}-2(NO_3)]^{2+}$ and 209.03 $[\mathbf{4}-2(NO_3)]^{2+}$ corresponding to **2**, **3** and **4**, respectively for the loss of two nitrate anions in each cases. To further support this fact for the formation of **2** from **3** and **4**, a reaction was performed between equimolar ratio of **3** and **4** in CD_3CN:D_2O mixture (1:1). This mixture gave rise to **2** within 6 h at room temperature which was monitored by ^1H NMR (Fig. 3).

^1H NMR was recorded for a mixture of $Pd(NO_3)_2$, bpy and ligand **1** at a ratio of 1:1:2 in DMSO-d_6, which showed spontaneous and quantitative formation of **2**. Thus the formation of targeted product is found to be most facile in this solvent. However, practical difficulty in isolation of the product from the high boiling solvent being not attractive, the suggested solvent of choice for the reaction is a mixture of CH_3CN and H_2O.

Table 1
Comparison between classical and one pot method for the synthesis of **2**.

Method	Step	Time	Temperature (°C)	Yield (%)
Classical	1st	1 h	60	92
	2nd	30 min	60	83
	3rd	1 h	80	92[a]
One pot	one	6 h	room temperature	95

[a] Over all yield is 70%.

2.2. One pot synthesis of the model complex [Pd(en)(4-phenylpyridine)$_2$](NO$_3$)$_2$, 5: unfeasible

When a similar reaction was tried for "en" instead of "bpy" in the most favorable system i.e. DMSO-d_6 at room temperature a mixture of product was resulted as **5**, **3** and **6** (Figs. 1 and 4). Formation of **5**, **3** and **6** was confirmed by comparing the ^1H NMR spectra of the pure compounds in DMSO-d_6. When ESI-MS for this reaction mixture was recorded it showed peaks at *m/z* = 238.00 $[\mathbf{5}-2(NO_3)]^{2+}$, 363.05 $[\mathbf{3}-2(NO_3)]^{2+}$, 287.97 $[\mathbf{6}-(NO_3)]^{+}$ and 113.00 $[\mathbf{6}-2(NO_3)]^{2+}$ which informed the presence of all the three compounds. Thus the one pot synthesis was found to be suitable for bpy system and not for the en system as observed from the study of the model complexes.

2.3. Theoretical study to understand the feasibility of bpy system versus unfeasibility of en system in one pot synthesis

Optimized structures were obtained at the B3LYP level of theory and with 6-31G(d) basis set for C, H, N and Lanl2dz for Pd in gas phase at 298.15 K (Fig. 5). Gibb's free energy for formation of **2**,

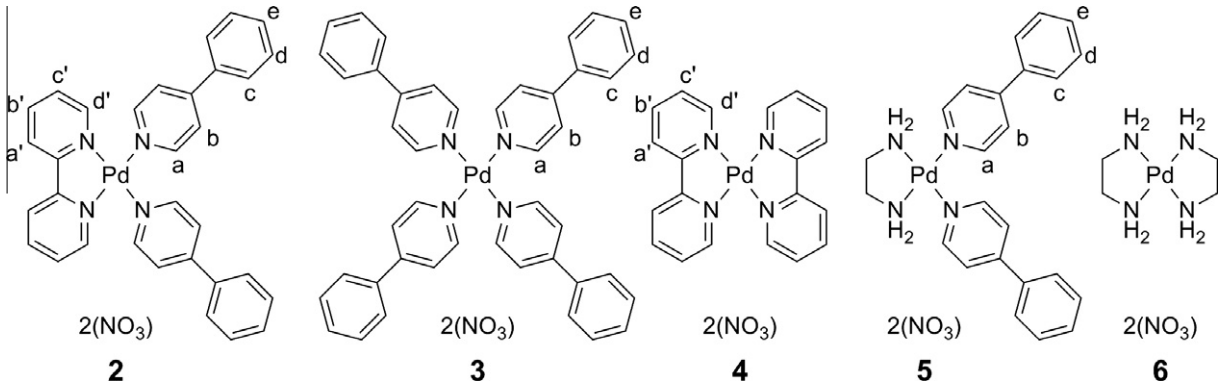


Fig. 1. Complexes **2**–**6**.

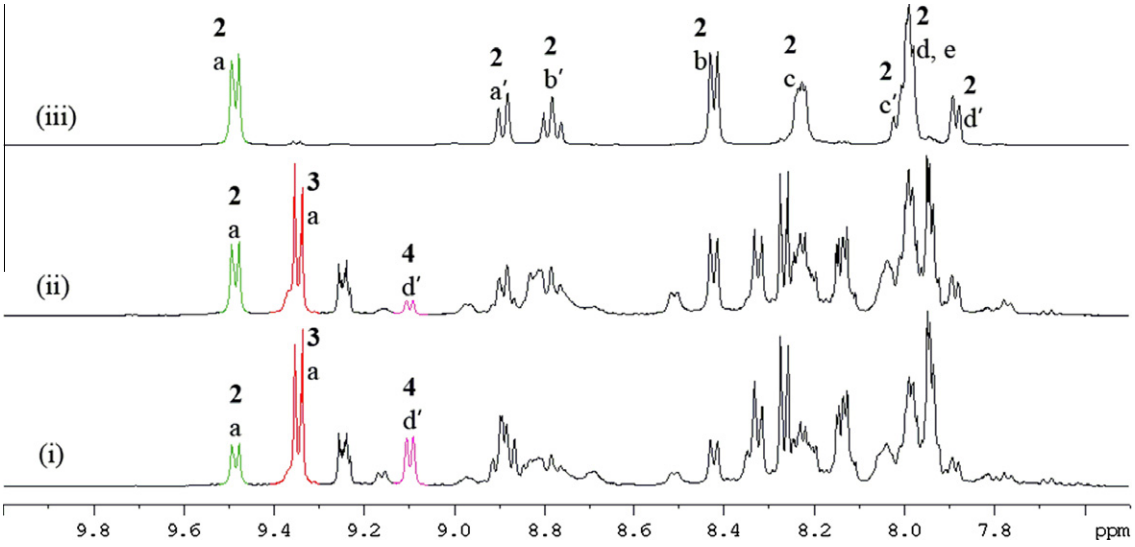


Fig. 2. ^{1}H NMR spectra in CD_3CN:D_2O (1:1) monitored in the process of the preparation of **2** by one pot synthesis at various time (i) t = 6 min; (ii) t = 20 min; (iii) t = 6 h; (py_α protons for **2** (green) and **3** (red); bpy_α **4** (pink)). (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

3, **4**, **5** and **6** from $Pd(NO_3)_2$ with corresponding ligands are 163.2, 157.51, 182.3, 170.99 and -197.1 kcal mol^{-1}, respectively, which indicate that none of these complexations are spontaneous except **6** which is dedicated to chelation. Enthalpy of formation for **2**, **3**, **4**, **5** and **6** are 149.2, 54.73, 177.85, 157.14 and 192.35 kcal mol^{-1}, respectively, which suggests the endothermic nature of all these complexation reactions.

The overall free energy and enthalpy for the formation of **2** from **3** and **4** Eq. (1) is −6.705 kcal mol^{-1} (spontaneous) and 32.91 kcal mol^{-1} (endothermic), respectively where as for formation of **5** from **3** and **6** Eq. (2) the values are 190.785 kcal mol^{-1} (non-spontaneous) and 33.6 kcalmol^{-1} (endothermic), respectively. This indicates that the reaction shown in Eq. (1) is favourable which may facilitate the one pot synthesis.

$$\mathbf{3} + \mathbf{4} \rightarrow \mathbf{2} \quad (1)$$

$$\mathbf{3} + \mathbf{6} \rightarrow \mathbf{5} \quad (2)$$

Also, the log K_1 and log K_2 for the formation of $[Pd(X{-}X)_2]^{2+}$ complexes are 23.6 and 18.6 for (en) whereas, the values are 19.8 and 8.9 for (bpy) [10] indicating higher stability of **6** as compared to **4**.

*2.4. X-ray crystal structure of the complexes **2**–**4***

The crystal structures of **2** and **3** are reported in this work where as that of **4** was reported earlier [11]. Single crystals of **2** were grown by diffusing benzene to an acetonitrile solution of the complex where as for the complex **3** tetrahydrofuran was diffused to an acetonitrile solution of the complex. The structures were solved by direct methods (SHELXL-97) and refined by full-matrix least squares methods on F^2 with 951 and 1566 parameters, respectively. Perspective view of the complexes are given in Figs. 6 and 7 where as the structural parameters and other details are collected in Table 2. After solving the crystal structure of **2**, a biphenyl kind of molecule was also found in the lattice. Thus the crystallization was performed by slow evaporation of water:acetonitrile (1:1) mixture where the same crystal system was observed . It was further supported by recording the ^{1}H NMR of these crystals which gave a clear idea about the free 4-phenylpyridine. During crystallization may be some amount of 4-phenylpyridine is dissociated from the complex to give a clathrate compound. Important bond distances and angles are given in Table 3 and 4 for crystal **2** and **3**, respectively.

The structure of **2** contains four cations of $[Pd(bpy)(\mathbf{1})_2]^{2+}$ and one 4-phenylpyridine on a centre of symmetry and two aceto-

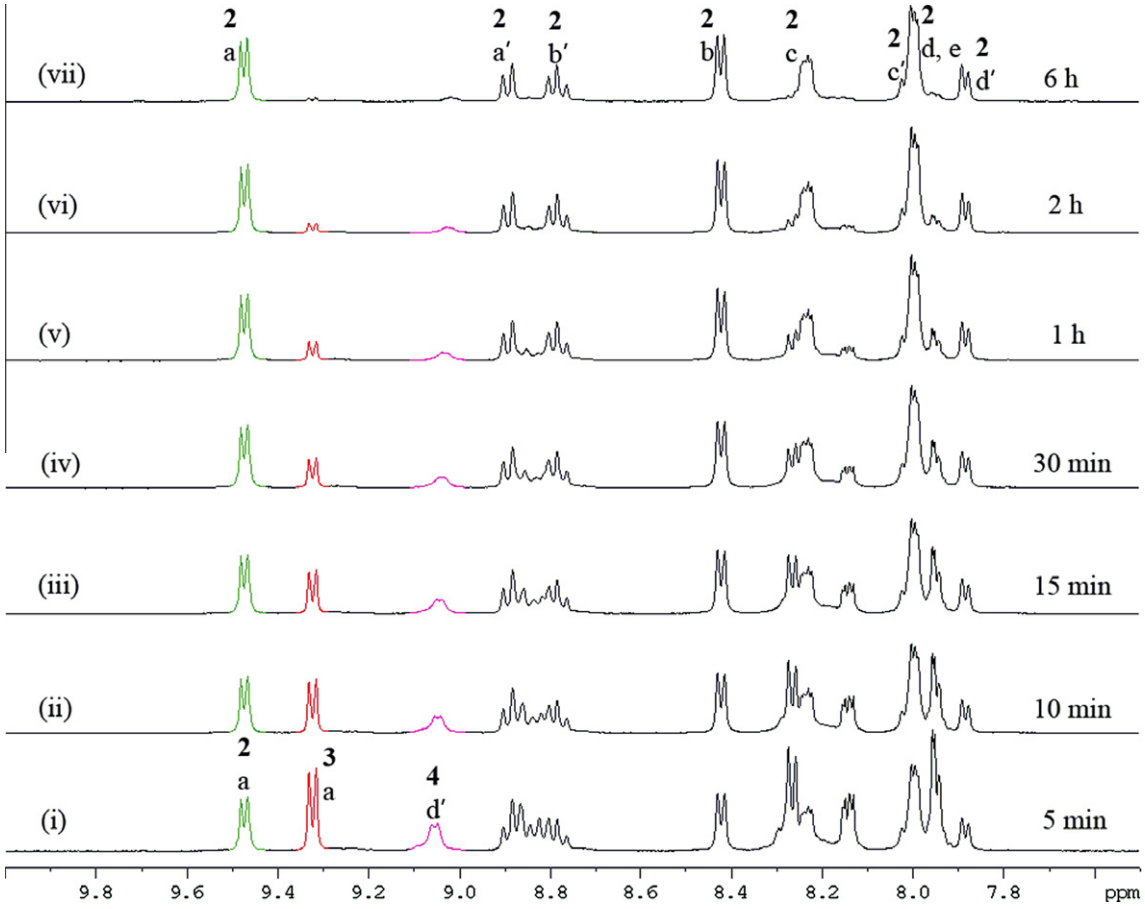


Fig. 3. ^{1}H NMR spectra for combination of **3** and **4** in CD_3CN:D_2O (1:1) to generate **2** at verious time interval (i) t = 5 min; (ii) t = 10 min; (iii) t = 15 min; (iv) t = 30 min; (v) t = 1 h; (vi) t = 2 h; (vii) t = 6 h; (py_α protons for **2** (green) and **3** (red); bpy_α **4** (pink)). (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

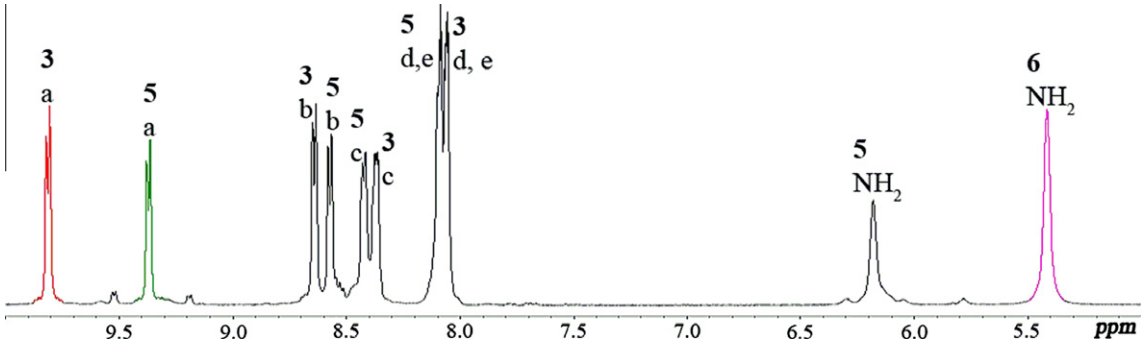


Fig. 4. ^{1}H NMR spectrum in DMSO-d_6 for the preparation of **5** by one pot synthesis (py_α protons for **5** (green) and **3** (red); en NH_2 for **6** (pink)). (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

nitrile as well as two water molecules in the unit cell (Fig. 6). Eight nitrate anions which corresponds to four Pd(II) are present in a unit cell. Out of four cations units of Pd(II) each pair exist as crystallographically different species. Each Pd(II) ion adopts a square planar geometry with Pd–N bond distances ranges from 2.002 to 2.024 Å. The bite angle of 2,2′-bipyridine with Pd(II) is 80.96° and 80.88° for N4–Pd1–N3 and N7–Pd2–N6, respectively. Angle between two pyridine units from 4-phenylpyridine attached to Pd(II) is 81.83° and each ligand unit remains perpendicular to the square plane of Pd(II). An acetonitrile molecule is distorted. There exist π···π stacking between 2,2′-bipyridine of one cation unit with 4-phenylpyridine of other cation unit of Pd(II) at a distance of 3.604 and 3.803 Å.

There are twelve cation units $[Pd(\mathbf{1})_4]^{2+}$ in a unit cell for the structure of **3** (Fig. 7). Twenty-four nitrate anions which corresponds to twelve Pd(II) unit and eight water molecules are present in a unit cell. There are three independent cation units of Pd(II) which are crystallographically different. Each Pd(II) ion adopts a square planar geometry with Pd–N bond distances ranges from 1.996 to 2.038 Å. Angle between two pyridine units from 4-phenylpyridine attached to Pd(II) is around 90° and each ligand unit remains perpendicular to the square plane of Pd(II). The crystal is stabilized by π···π and CH···π interactions. There exist π···π stacking between 4-phenylpyridine of one cation unit with other cation unit at a distance of 3.961 Å. There also exist a CH···π interaction between 4-phenylpyridine of one cation unit with

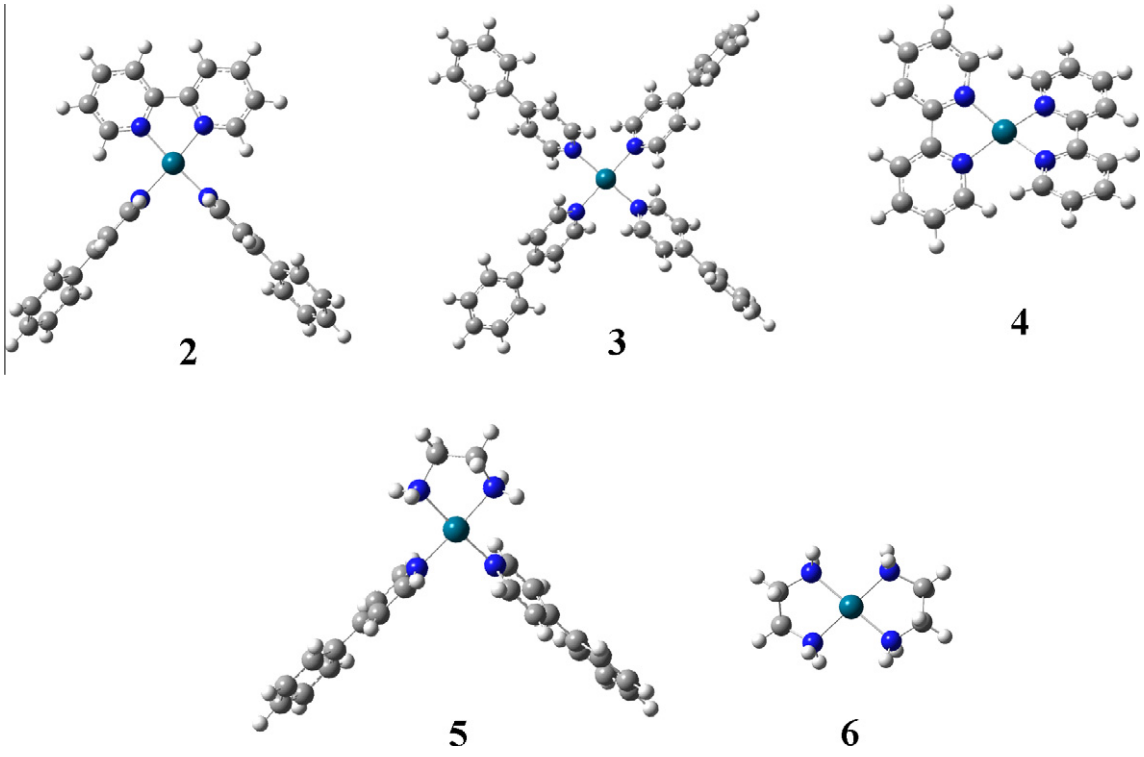


Fig. 5. Optimised structures of the complexes **2–6**.

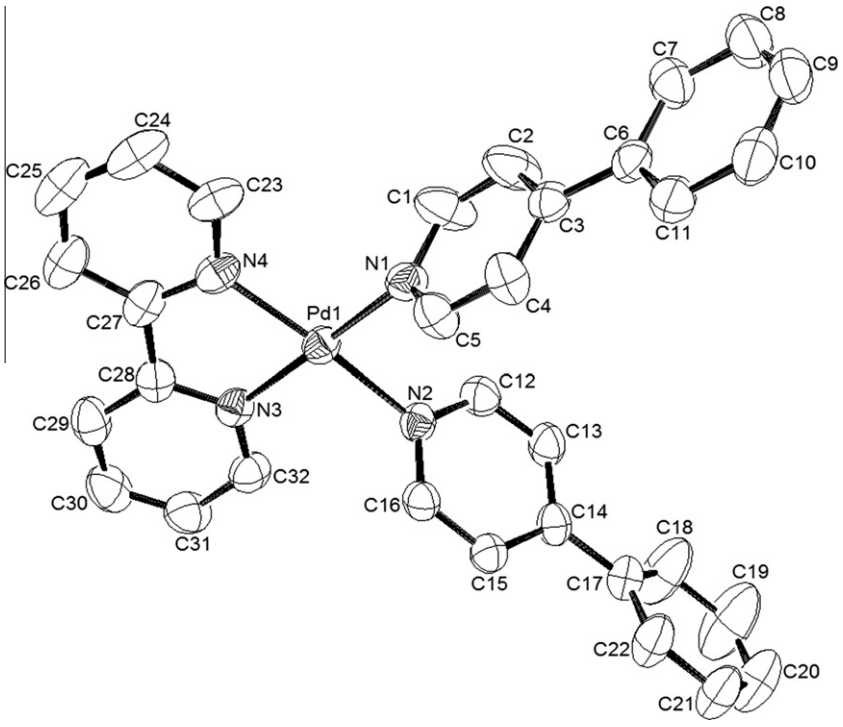


Fig. 6. ORTEP diagram showing the complexed cation $[Pd(bpy)(4\text{-phenylpyridine})_2]^{2+}$ (other fragments are omitted for clarity).

other cation unit at a distance of 3.761 Å. One of the nitrate has short contact at a distance of 3.126 Å with the fifth coordination site of Pd(II). Hydrogen bonding exist between oxygen of nitrate and CH of 4-phenylpyridine. Oxygen of two different nitrates are connected through hydrogen bonding with one water molecule.

As per the reported data [11] the geometry around Pd(II) in $[Pd(bpy)_2](NO_3)_2$, **4** is severely distorted from the square planar geometry where the dihedral angle between the planes of the two bpy unit is as large as 33° due to the steric repulsions making it unfavourable.

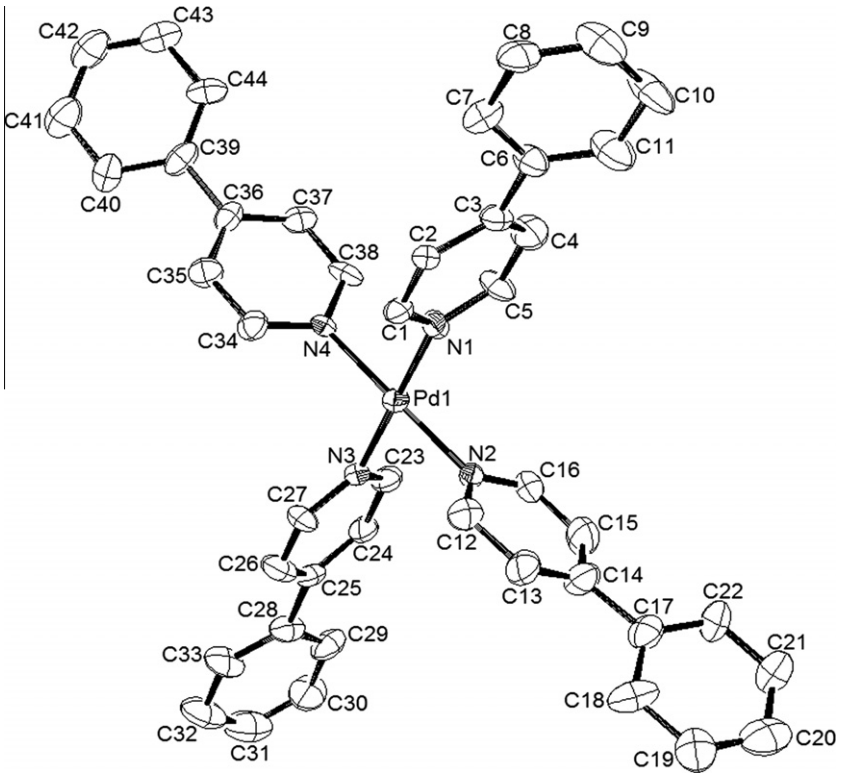


Fig. 7. ORTEP diagram showing the complexed cation $[Pd(4\text{-phenylpyridine})_4]^{2+}$ (other fragments are omitted for clarity).

Table 2
Crystal data and structure refinement parameters for **2** and **3**.

Compounds	**2**·1/4($C_{11}H_9N$)·1/2(C_2H_3N)·1/2(H_2O)·3/2(O)	**3**·1/3·(H_2O·O)
Empirical formula	$C_{143}H_{123}N_{27}O_{32}Pd_4$	$C_{132}H_{110}N_{18}O_{20}Pd_3$
Formula weight	3157.28	2587.58
Crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a (Å)	13.2612 (3)	25.595 (2)
b (Å)	15.7740 (4)	18.480 (2)
c (Å)	17.4441 (5)	25.803 (3)
α (°)	83.674 (1)	90
β (°)	82.025 (1)	94.796 (4)
γ (°)	73.465 (1)	90
Volume (Å)^3	3454.64 (15)	12162 (2)
Z	1	4
Wavelength (Å)	0.71073	0.71073
Temperature (K)	173 (2)	173 (2)
Calculated density (g/cm^3)	1.518	1.413
Absorption coefficient (mm^{-1})	0.60	0.52
F(0 0 0)	1610	5304
Crystal dimensions (mm)^3	0.42 × 0.38 × 0.27	0.28 × 0.25 × 0.22
θ Range for data collection (°)	2.0–28.4	1.4–28.3
Limiting indices	$-17 \leqslant h \leqslant 12$, $-21 \leqslant k \leqslant 20$, $-21 \leqslant l \leqslant 23$	$-24 \leqslant h \leqslant 34$, $-20 \leqslant k \leqslant 24$, $-30 \leqslant l \leqslant 34$
Reflections collected/unique	45 848/15 202	81 737/28 342
Data/restraints/parameter	15 202/8/951	28 342/0/1566
Goodness-of-fit (GOF) on F	1.053	1.057
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0529 wR_2 = 0.1502	R_1 = 0.1109 wR_2 = 0.3030
R indices (all data)	R_1 = 0.0841 wR_2 = 0.1781	R_1 = 0.2083 wR_2 = 0.3677
CCDC	CCDC 795973	CCDC 795974

Table 3
Selected bond lengths (Å) and bond angles (°) for **2**·1/4($C_{11}H_9N$)·1/2(C_2H_3N)·1/2(H_2O)·3/2(O).

N1—Pd1	2.024
N2—Pd1	2.018
N3—Pd1	2.016
N4—Pd1	2.012
N5—Pd2	2.016
N6—Pd2	2.016
N7—Pd2	2.002
N8—Pd2	2.022
N9—O1	1.220
N9—O3	1.223
N9—O2	1.227
N4—Pd1—N3	80.96
N4—Pd1—N2	176.51
N3—Pd1—N2	96.09
N4—Pd1—N1	96.80
N3—Pd1—N1	175.77
N2—Pd1—N1	86.03
N7—Pd2—N6	80.88
N7—Pd2—N5	176.21
N6—Pd2—N5	96.40
N7—Pd2—N8	96.00
N6—Pd2—N8	171.22
N5—Pd2—N8	87.07

3. Conclusion

Synthesis of a class of Pd(II) compounds namely $[\{Pd(bpy)\}_x(\mathbf{L})_y](NO_3)_{2x}$ by an alternative and more efficient one pot technique is modeled by using 4-phenylpyridine as a ligand. The thermodynamically favored product $[Pd(bpy)(4\text{-phenylpyridine})_2](NO_3)_2$ is formed exclusively by simply combining $Pd(NO_3)_2$, bpy and 4-phenylpyridine at a required ratio under optimized reaction conditions.

Table 4
Selected bond lengths (Å) and bond angles (°) for **3**·1/3·(H_2O·O).

N1—Pd1	2.0270
N2—Pd1	2.0195
N3—Pd1	2.0270
N4—Pd1	2.0135
N5—Pd2	2.0106
N6—Pd2	2.0111
N7—Pd2	2.0132
N8—Pd2	2.0149
N9—Pd3	1.9965
N10—Pd3	2.0147
N11—Pd3	2.0381
N12—Pd3	2.0009
N1—Pd1—N3	178.2
N2—Pd1—N3	88.7
N2—Pd1—N1	90.6
N4—Pd1—N1	88.9
N4—Pd1—N2	179.2
N4—Pd1—N3	91.8
N5—Pd2—N6	88.8
N5—Pd2—N7	179.4
N5—Pd2—N8	91.0
N6—Pd2—N7	91.2
N6—Pd2—N8	179.2
N7—Pd2—N8	89.0
N9—Pd3—N10	88.2
N9—Pd3—N11	177.6
N9—Pd3—N12	91.4
N10—Pd3—N11	91.6
N12—Pd3—N10	179.4
N12—Pd3—N11	88.8

4. Experimental

4.1. General

$PdCl_2$, $Pd(NO_3)_2$, 4-phenylpyridine and 2,2′-bipyridine were obtained from Aldrich whereas ethylenediamine, $AgNO_3$ and the usual solvents were obtained from Spectrochem, India. The deuterated solvents D_2O, CD_3CN and DMSO-d_6 were obtained from Cambridge Isotope Laboratories. The *cis*-protected Pd(II) components i.e. *cis*-[Pd(bpy)$(NO_3)_2$] and *cis*-[Pd(en)$(NO_3)_2$] were prepared by known methods. The assemblies [Pd(bpy)-(4-phenylpyridine)$_2$]$(NO_3)_2$, **2** was prepared by us earlier by classical method and now by the alternative one pot approach. The related complexes [Pd(4-phenylpyridine)$_4$]$(NO_3)_2$, **3**; and [Pd(en)(4-phenylpyridine)$_2$]$(NO_3)_2$, **5** were prepared by reported method [12] and [Pd(bpy)$_2$][$(NO_3)_2$], **4**; [Pd(en)$_2$][$(NO_3)_2$], **6** were prepared according to the literature procedures [7]. ^{1}H NMR spectra were recorded on a Bruker 400 MHz FT NMR instrument using TMS/$CDCl_3$ as external standard. The ^{1}H NMR spectral data of the compounds in DMSO-d_6 are available in literature. However, for the purpose of the present study NMR data was obtained in CD_3CN:D_2O (1:1) and provided here for the compounds **2**, **3** and **4**. The NMR data of the complexes **2**, **3**, **5** and **6** in DMSO-d_6 is also provided for comparison purpose. The mass spectra of the samples of **2** and **3** were obtained from a Micromass Q-ToF mass spectrometer by electrospray ionisation method. The single crystal X-ray analysis for **2** and **3** were carried out using a Bruker X8 Kappa XRD instrument. Elemental analysis was performed on Perkin–Elmer 2400 series CHNS/O Analyser.

4.2. Synthesis of [Pd(bpy)(4-phenylpyridine)$_2$]$(NO_3)_2$, **2**

(a) *Classical method:* preparation of Pd(bpy)Cl_2 which is also commercially available was carried out by adding bpy to a hot acetonitrile solution of $PdCl_2$ following literature procedure [8]. The chloride anion was exchanged with nitrate by reacting Pd(bpy)Cl_2 with $AgNO_3$ in aq HNO_3 at pH 1 [8]. Thus formed Pd(bpy)$(NO_3)_2$ (0.0193 g, 0.05 mmol) was suspended in 5 mL of CH_3CN and 4-phenylpyridine (0.0155 g, 0.1 mmol) was added to it. The mixture was refluxed for 1 h with continuous stirring then it was cooled down to room temperature. The yellowish solution was evaporated and dried under vacuum to obtain the complex **2** as a yellow solid (0.0319 g, 92% yield) [7]. The overall calculated yield is 70%.

(b) *One pot method:* 2,2′-bipyridine (0.0078 g, 0.05 mmol) and 4-phenylpyridine (0.0155 g, 0.1 mmol) was dissolved in 5 mL of CH_3CN:H_2O (1:1). To this solution $Pd(NO_3)_2$ (0.0138 g, 0.06 mmol) was added and stirred for 6 h at room temperature. The pale coloured solution was evaporated by N_2 fluxing and dried under vacuum. The solid was washed with ether and dried again to afford a pale yellow solid as the product (0.0332 g, yield 95%).

4.3. Analytical data of the complexes **2**–**6**

4.3.1. [Pd(bpy)(4-phenylpyridine)$_2$]$(NO_3)_2$, **2**

^{1}H NMR (400 MHz, DMSO-d_6, external TMS/$CDCl_3$): δ 9.84 (d, J = 6.2 Hz, 4H, a), 9.34 (d, J = 8.0 Hz, 2H, a′), 9.05 (t, J = 8.4 Hz, 2H, b′), 8.75 (d, J = 6.6 Hz, 4H, b), 8.48 (d, J = 3.6 Hz, 4H, c), 8.28 (t, J = 6.4 Hz, 2H, c′), 8.10–8.13 (m, 8H, d, e and d′) ppm. ^{1}H NMR (400 MHz, CD_3CN:D_2O (1:1), external TMS/$CDCl_3$): δ 9.47 (d, J = 5.9 Hz, 4H, a), 8.89 (d, J = 8.0 Hz, 2H, a′), 8.78 (t, J = 8.0 Hz, 2H, b′), 8.42 (d, J = 5.8 Hz, 4H, b), 8.24–8.22 (m, 4H, c), 8.02–7.99 (m, 8H, c′, d and e), 7.88 (d, J = 5.6 Hz, 2H, d′) ppm. ESI-MS: *m/z* 286.1 for [**2**−2(NO_3)]$^{2+}$. *Anal.* Calc. for $C_{32}H_{26}N_6O_6Pd$ (697.00): C, 55.14; H, 3.76; N, 12.06. Found: C, 55.28; H, 3.90; N, 11.9%.

4.3.2. [Pd(4-phenylpyridine)$_4$]$(NO_3)_2$, **3**

^{1}H NMR (400 MHz, DMSO-d_6, external TMS/$CDCl_3$): δ 9.81 (d, J = 6.1 Hz, 8H, a), 8.64 (d, J = 6 Hz, 8H, b), 8.38–8.36 (m, 8H, c), 8.07–8.06 (m, 12H, d and e) ppm. ^{1}H NMR (400 MHz, CD_3CN:D_2O (1:1), external TMS/$CDCl_3$): δ 9.33 (d, J = 6.4 Hz, 8H, a), 8.26 (d, J = 6.4 Hz, 8H, b), 8.15–8.13 (m, 8H, c), 7.95–7.94 (m, 12H, d and e) ppm. ESI-MS: *m/z* 363.04 for [**3**−2(NO_3)]$^{2+}$. *Anal.* Calc. for $C_{44}H_{36}N_6O_6Pd$ (851.21): C, 62.08; H, 4.26; N, 9.87. Found: C, 61.85; H, 4.42; N, 10.11%.

4.3.3. [Pd(bpy)$_2$][$(NO_3)_2$], **4**

^{1}H NMR (400 MHz, CD_3CN:D_2O (1:1), external TMS/$CDCl_3$): δ 9.10 (d, J = 5.6 Hz, 4H, d′), 8.91–8.84 (m, 8H, a′ and b′), 8.32 (t, J = 6.8 Hz, 4H, c′) ppm.

4.3.4. [Pd(en)(4-phenylpyridine)$_2$]$(NO_3)_2$, **5**

^{1}H NMR (400 MHz, DMSO-d_6, external TMS/$CDCl_3$): δ 9.37 (d, J = 6.0 Hz, 4H, a), 8.57 (d, J = 6.2 Hz, 4H, b), 8.43–8.41 (m, 4H, c), 8.07–8.06 (m, 6H, d and e), 6.18 (s, 4H, –NH_2), 3.23 (s, 4H, –CH_2) ppm.

4.3.5. [Pd(en)$_2$][$(NO_3)_2$], **6**

^{1}H NMR (400 MHz, DMSO-d_6, external TMS/$CDCl_3$): δ 5.42 (s, 4H, NH_2) ppm, CH_2 peak is merged with DMSO-d_6.

Acknowledgments

This study was supported by a grant in aid for scientific research from the Department of Science and Technology (DST), New Delhi, India (No. SR/S1/IC-28/2009). We thank Dr. S. Suvitha and Dr. N.S. Venkataramanan for helping us in theoretical calculations.

Appendix A. Supplementary material

CCDC 795973 and 795974 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.02.009.

References

[1] J.W. Steed, J.L. Atwood, in: Supramolecular Chemistry, second ed., John Wiley and Sons, Ltd., 2009.

[2] (a) D.K. Chand, K. Biradha, M. Fujita, S. Sakamoto, K. Yamaguchi, Chem. Commun. (2002) 2486;
(b) M. Tominaga, K. Suzuki, M. Kawano, T. Kusukawa, T. Ozeki, S. Sakamoto, K. Yamaguchi, M. Fujita, Angew. Chem., Int. Ed. 43 (2004) 5621;
(c) A. Hori, K. Yamashita, T. Kusukawa, A. Akasaka, K. Biradha, M. Fujita, Chem. Commun. (2004) 1798;
(d) N.L.S. Yue, D.J. Eisler, M.C. Jennings, R.J. Puddephatt, Inorg. Chem. 43 (2004) 7671;
(e) K. Suzuki, M. Kawano, M. Fujita, Angew. Chem., Int. Ed. 46 (2007) 2819;
(f) M. Fukuda, R. Sekiya, R. Kuroda, Angew. Chem., Int. Ed. 47 (2008) 706;
(g) K. Suzuki, M. Tominaga, M. Kawano, M. Fujita, Chem. Commun. (2009) 1638;
(h) H.S. Sahoo, D.K. Chand, Dalton Trans. 39 (2010) 7223.

[3] (a) M. Yoshizawa, M. Fujita, Bull. Chem. Soc. Jpn. 83 (2010) 609;
(b) R.S. Forgan, D.C. Friedman, C.L. Stern, C.J. Bruns, J.F. Stoddart, Chem. Commun. 46 (2010) 5861;
(c) P.J. Stang, B. Olenyuk, Acc. Chem. Res. 30 (1997) 502;
(d) S.R. Seidel, P.J. Stang, Acc. Chem. Res. 35 (2002) 972;
(e) G.F. Swiegers, T.J. Malefetse, Coord. Chem. Rev. 225 (2002) 91;
(f) M. Fujita, M. Tominaga, A. Hori, B. Therrien, Acc. Chem. Res. 38 (2005) 371.

[4] (a) M. Fujita, F. Ibukuro, H. Hagihara, K. Ogura, Nature 367 (1994) 720;
(b) S.B. Lee, S. Hwang, D.S. Chung, H. Yun, J.-I. Hong, Tetrahedron Lett. 39 (1998) 873;
(c) G. Ma, Y.S. Jung, D.S. Chung, J.-I. Hong, Tetrahedron Lett. 40 (1999) 531;
(d) S. Hiraoka, M. Fujita, J. Am. Chem. Soc. 121 (1999) 10239;
(e) A. Sautter, D.G. Schmid, G. Jung, F. Würthner, J. Am. Chem. Soc. 123 (2001) 5424;
(f) A. Hori, K. Kumazawa, T. Kusukawa, D.K. Chand, M. Fujita, S. Sakamoto, K. Yamaguchi, Chem. Eur. J. 7 (2001) 4142;
(g) Y. Yamanoi, Y. Sakamoto, T. Kusukawa, M. Fujita, S. Sakamoto, K. Yamaguchi, J. Am. Chem. Soc. 123 (2001) 980;
(h) C.A. Schalley, T. Müller, P. Linnartz, M. Witt, M. Schäfer, A. Lützen, Chem. Eur. J. 8 (2002) 3538;
(i) A. Hori, A. Akasaka, K. Biradha, S. Sakamoto, K. Yamaguchi, M. Fujita, Angew. Chem., Int. Ed. 41 (2002) 3269;
(j) M. Schweiger, S.R. Seidel, A.M. Arif, P.J. Stang, Inorg. Chem. 41 (2002) 2556;
(k) M. Ferrer, M. Mounir, O. Rossell, E. Ruiz, M.A. Maestro, Inorg. Chem. 42 (2003) 5890;
(l) S. Tashiro, M. Tominaga, T. Kusukawa, M. Kawano, S. Sakamoto, K. Yamaguchi, M. Fujita, Angew. Chem., Int. Ed. 42 (2003) 3267;
(m) T. Yamamoto, A.M. Arif, P.J. Stang, J. Am. Chem. Soc. 125 (2003) 12309;
(n) A. Hori, T. Sawada, K. Yamashita, M. Fujita, Angew. Chem., Int. Ed. 44 (2005) 4896;
(o) S.J. Park, D.M. Shin, S. Sakamoto, K. Yamaguchi, Y.K. Chung, M.S. Lah, J.-I. Hong, Chem. Eur. J. 11 (2005) 235;
(p) D.K. Chand, K. Biradha, M. Kawano, S. Sakamoto, K. Yamaguchi, M. Fujita, Chem. Asian J. (1–2) (2006) 82;
(q) K. Uehara, K. Kasai, N. Mizuno, Inorg. Chem. 46 (2007) 2563;
(s) S. Ghosh, P.S. Mukherjee, Inorg. Chem. 48 (2009) 2605;
(t) K. Uehara, K. Kasai, N. Mizuno, Inorg. Chem. 49 (2010) 2008.

[5] (a) M. Fujita, O. Sasaki, T. Mitsuhashi, T. Fujita, J. Yazaki, K. Yamaguchi, K. Ogura, Chem. Commun. (1996) 1535;
(b) J.A.R. Navarro, M.A. Romero, J.M. Salas, J. Chem. Soc., Dalton Trans. (1997) 1001;
(c) F. Ibukuro, M. Fujita, K. Yamaguchi, J.-P. Sauvage, J. Am. Chem. Soc. 121 (1999) 11014;
(d) B. Oskui, W.S. Sheldrick, Eur. J. Inorg. Chem. (1999) 1325;
(e) T. Kusukawa, M. Fujita, J. Am. Chem. Soc. 124 (2002) 13576;
(f) M. Abul-Haj, M. Quirós, J.M. Salas, J. Chem. Soc., Dalton Trans. (2002) 4740;
(g) M. Abul-Haj, M. Quirós, J.M. Salas, Polyhedron 23 (2004) 2373;
(h) S.-Y. Yu, H.-P. Huang, S.-H. Li, Q. Jiao, Y.-Z. Li, B. Wu, Y. Sei, K. Yamaguchi, Y.-J. Pan, H.-W. Ma, Inorg. Chem. 44 (2005) 9471;
(i) H.-P. Huang, S.-H. Li, S.-Y. Yu, Y.-Z. Li, Q. Jiao, Y.-J. Pan, Inorg. Chem. Commun. 8 (2005) 656;
(j) M. Ferrer, A. Gutiérrez, M. Mounir, O. Rossell, E. Ruiz, A. Rang, M. Engeser, Inorg. Chem. 46 (2007) 3395;;
(k) S. Ghosh, R. Chakrabarty, P.S. Mukherjee, Dalton Trans. (2008) 1850;
(l) Q.-F. Sun, K. M.-C. Wong, L.-X. Liu, H.-P. Huang, S.-Y. Yu, V.W.-W. Yam, Y.-Z. Li, Y.-J. Pan, K.-C. Yu, Inorg. Chem. 47 (2008) 2142;;
(m) E. Gao, M. Zhu, H. Yin, L. Liu, Q. Wu, Y. Sun, J. Inorg. Biochem. 102 (2008) 1958;
(n) W.-Z. Shen, G. Trötscher-Kaus, B. Lippert, Dalton Trans. (2009) 8203;
(o) A. Rotondo, G. Bruno, M. Cusumano, E. Rotondo, Inorg. Chim. Acta 362 (2009) 4767;
(p) D. Schilter, J.K. Clegg, M.M. Harding, L.M. Rendina, Dalton Trans. 39 (2010) 239;
(q) G.-H. Ning, T.-Z. Xie, Y.-J. Pan, Y.-Z. Li, S.-Y. Yu, Dalton Trans. 39 (2010) 3203;
(r) A. Khutia, P.J.S. Miguel, B. Lippert, Inorg. Chem. 49 (2010) 7635.

[6] N.B. Debata, D. Tripathy, V. Ramkumar, D.K. Chand, Tetrahedron Lett. 51 (2010) 4449.

[7] H.S. Sahoo, D.K. Chand, N.B. Debata, Inorg. Chim. Acta 360 (2007) 31.

[8] S. Wimmer, P. Castan, F.L. Wimmer, N.P. Johnson, J. Chem. Soc., Dalton Trans. (1989) 403.

[9] J. Athilakshmi, S. Ramanathan, D.K. Chand, Tetrahedron Lett. 49 (2008) 5286.

[10] G. Anderegg, H. Wanner, Inorg. Chim. Acta 113 (1986) 101.

[11] (a) M. Hinamoto, S. Ooi, H. Kuroya, J. Chem. Soc., Chem. Commun. (1972) 356;
(b) P.C. Chieh, J. Chem. Soc., Dalton Trans. (1972) 1643.

[12] D.K. Chand, R. Manivannan, H.S. Sahoo, K. Jeyakumar, Eur. J. Inorg. Chem. (2005) 3346.