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SYNTHESIS, STRUCTURAL AND SPECTROSCOPIC STUDIES OF PALLADIUM(II) METALLO-MACROCYLES CONTAINING ANCILLARY BLOCKING LIGANDS AND *N,N'*-2,6-*BIS*(3-PYRIDYLMETHYL)PYRIDINE DICARBOXAMIDE

(Sintesis, Struktur Dan Kajian Spektroskopik Makrosiklik-Berlogam Paladium(II) Terkandung Ligan Sampingan dan 2,6-*Bis*(3-Piridilmetil)Piridin Dikarbosamida)

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Abstract

Reaction between *N,N'*-2,6-*bis*(3-pyridylmethyl)pyridine dicarboxamide (**L**) with dichloropalladium(II) 2,2'-bipyridine [$PdCl_2$(2,2'-bipy)] and dichloropalladium(II) ethylenediamine [$PdCl_2$(en)] gave rise to two novel metallo-macrocycles, [Pd(**L**)(2,2'-bipy)]$(PF_6)_2$ (**A1**) and **[**Pd(en)(**L**)]$(PF_6)_2 \cdot H_2O \cdot 2CH_3OH$ (**A2**), respectively. These complexes were characterized by spectroscopic techniques such as Fourier Transform Infrared (FT-IR), Nuclear Magnetic Resonance (NMR), electrospray ionization mass spectrometry (ESI-MS) and elemental analysis. The studies on the interactions between the protons of the ligand and the protons of the ancillary ligands (etc. bipy, en) of the complexes were identified by using two dimensional NMR techniques such as Nuclear Overhauser Spectroscopy (2D NOESY) and correlation spectroscopy (COSY). X-ray crystallography shows that complex **A2** form a bowl-like structure with one hexafluorophosphate anions encapsulated in the molecule cavity. The hexafluorophosphate anions form weak interaction with the ancillary ligand ethylenediamine (N-H···F, d = 2.379, D = 3.113 Å) which stabilized by weak C-H···F hydrogen bonding. The presence of weak anion-π contact is also observed between the anion and the central pyridine of the metallo-macrocycle. Further analysis by diffusion-ordered spectroscopy (DOSY) has shown that the diffusion rates of complexes **A1** and **A2** are lower from the theoretical value. This might be due to the complexing of hexafluorophosphate anions that increase the hydrodynamic radii of the complexes.

Keywords: flexible, anion-π, hydrogen bonding, palladium, metallo-macrocycles

Abstrak

Tindak balas antara ligan 2,6-*bis*(3-piridilmetil)piridin dikarbosamida (**L**) dengan dikloropaladium(II) 2,2'-bipiridin[$PdCl_2$(2,2'-bipy)] dan dikloropaladium(II) etilenadiamina [$PdCl_2$(en)] telah memberikan dua makrosiklik- berlogam yang baru, masing-masing sebagai [Pd(**L**)(2,2'-bipy)]$(PF_6)_2$ (**A1**) dan **[**Pd(en)(**L**)]$(PF_6)_2 \cdot H_2O \cdot 2CH_3OH$ (**A2**). Kompleks ini telah dicirikan dengan kaedah spektroskopi seperti Fourier Pengubah Inframerah (FT-IR), Nukleus Magnetik Resonan (NMR), elektrosemburan pengionan spektrometri jisim (ESI-MS) and analisis unsur. Kajian interaksi antara proton terhadap ligan serta proton terhadap ligan sampingan (seperti bipy, en) dalam kompleks dikenalpasti dengan menggunakan teknik NMR dua dimensi seperti spektroskopi Nuklear Overhauser (2D NOESY) dan spektroskopi Korelasi (COSY). Kajian X-ray kristalografi menunjukkan bahawa kompleks **A2** membentuk struktur mangkuk dengan satu anion heksafluorofosfat terperangkap dalam kaviti molekul. Anion heksafluorofosfat membentuk ikatan lemah dengan ko-ligan etilenadiamina (N-H···F, d = 2.379, D = 3.113 Å) dan distabilkan oleh ikatan hidrogen C-H···F. Kehadiran ikatan lemah anion-π juga dilihat di antara anion dengan pusat piridin makrosiklik-berlogam itu. Analisis seterusnya menggunakan spektroskopi sebaran turutan (DOSY) menunjukkan kadar sebaran yang rendah oleh **A1** dan **A2** berbanding nilai teori. Ini mungkin disebabkan oleh pengkompleksan anion heksafluorofosfat yang meningkatkan jejari hidrodinamik kompleks tersebut.

Kata kunci: ligan, ikatan anion-π, ikatan hidrogen, palladium, makrosiklik-berlogam

Introduction

Self-assembly by anion templation has been reported for a significant number of metallo-supramolecular assemblies [1-4]. This includes discrete circular helicates, [5] coordination nanotubes, [6] and polyhedral assemblies [7-8]. In the context of identifying new motifs for anion binding, such self-assembling species are attractive since the structural and functional properties of metal centres can be combined with the recognition properties of the organic hosts to obtain the target host systems [9]. Among of all strategies, combination of palladium(II) with organic linker is the most common in the design of anion host [10, 11]. Yu and co-workers for example, have currently synthesized two types of 'molecular basket organo-palladium' from combination of palladium(II) and phenanthroline that can encapsulate a large anion species such as cobalticarborane in water [11]. This study in particular has prompted us to continue our research in producing novel metallosupramolecular cages for anion inclusion [12-15, 21]. To generate simple and large palladium(II) metallosupramolecular assemblies for anions, this research utilizes the diamide ligand (**L**), namely *N,N'*-2,6-*bis*(3-pyridylmethyl)pyridine dicarboxamide (Figure 1) which was reacted with palladium metal salts that have two exchangeable coordination sites in a *cis* arrangement.

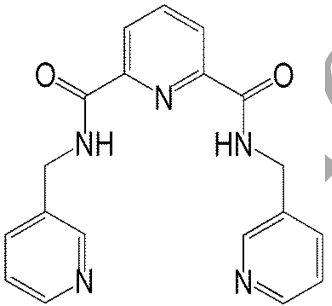
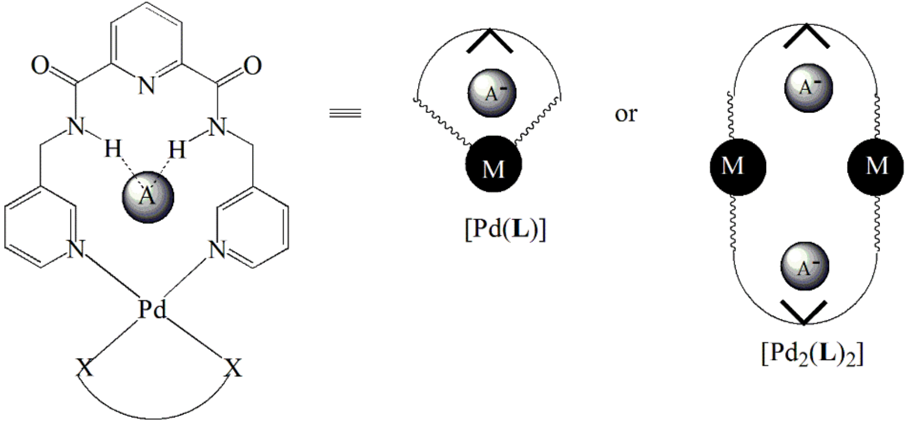


Figure 1. The structure of ligand *N,N'*-2,6-bis(3-pyridylmethyl)pyridine dicarboxamide.



A = anion, M= Pd and XX= en or bipy
L = ligand

Figure 2. A diagram representing the structures of simple mononuclear or dinuclear metallosupramolecular macrocycles proposed for reactions of ligand **L** with [$PdCl_2$(2,2'-bipy)] and [$PdCl_2$(en)].

It was anticipated that two products could be obtained from each of these reactions, specifically a mononuclear complex [Pd(**L**)] or a dinuclear [Pd_2(**L**)$_2$] species (Figure 2). Such species might provide useful anion binding regions due to the pre-organized hydrogen bond donor pockets of the ligand and an electrostatic contribution to anion binding provided by the palladium(II) center. In this account, the synthesis, characterization and evaluation on the spectroscopic studies particularly from 2D NMR techniques will be delineated. The coordination chemistry of the ligand with palladium ion along with supramolecular interactions that occur in the crystal structure of complex **A2** will also be described.

Materials and Methods

Melting points were measured on a Gallenkamp melting point apparatus and are uncorrected. Elemental analyses were performed by the Campbell Microanalytical Laboratory at the University of Otago, Dunedin, New Zealand. Infrared spectra were collected on a Perkin Elmer Spectrum BX Infrared spectrometer as KBr disks, or a Perkin Elmer Spectrum 100 using a Universal Attenuated Total Reflectance (UATR) sampling accessory. Nuclear magnetic resonances (NMR) spectra were recorded on Varian Gemini 300MHz NMR spectrometer or a Varian Inova 600 MHz NMR spectrometer at 23 ºC using a 5mm probe. ^{1}H NMR spectra recorded in deuterated dimethylsulfoxide (DMSO-d_6); ^{1}H NMR spectra recorded in DMSO-d_6 were referenced to the solvent peak: 2.6 ppm. ^{13}C NMR spectra were all referenced to their solvent peaks: DMSO, 39.6 ppm. When required, two dimensional correlation spectroscopy (2D COSY), two dimensional nuclear overhouser effect spectroscopy (2D NOESY) and two dimensional diffusion ordered spectroscopy (2D DOSY) experiments were performed using standard pulse sequences. Unless otherwise stated, the values given for chemical shifts are to the centre of a multiplet. Electrospray (ES) mass spectra were recorded using a Finnigan LCQ mass spectrometer by preparing serial dilutions of a 1 mg/mL solution of the compound.

Single Crystal X-ray Crystallography

Crystals were mounted under paratone-N oil on a plastic loop. X-ray diffraction datasets were collected with Mo-Kα radiation (λ = 0.71073 Å) using a Bruker-AXS Single Crystal Diffraction System fitted with an Apex II CCD detector at 110(2) K. All datasets were corrected for absorption using a multi-scan method, and structures were solved by direct methods using SHELXS-97 [16] and refined by full-matrix least squares on F^2 by SHELXL-97, [17] interfaced through the program X-Seed. [18] In general, all non-hydrogen atoms were refined anisotropically and hydrogen atoms were included as invariants at geometrically estimated positions, unless specified otherwise in additional details. Figures were produced using the program POV-Ray, [19] interfaced through the program X-Seed. Publication materials were prepared using CIFTAB. [20] Crystal data and structure refinement for complex **A2** is described as follow:

Crystal data for complex **A2** : $C_{22}\,H_{26}\,F_{12}\,N_7\,O_6\,P_2$ Pd, Mr = 880.84, monoclinic, space group P21/n, a = 13.7360(10) Å, b = 10.8580(9) Å, c = 21.6696(19) Å, β= 91.173(3)°, V = 3231.2(5) Å^3, Z = 4, T = 298K, D_{calcd} = 1.811 Mg/ml^3, μ = 0.792 mm^{-1}, GOOF = 1.064, R1(wR2) = 0.0489(0.1170). CCDC 1027221 contains the supplementary crystallographic data for these structures. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

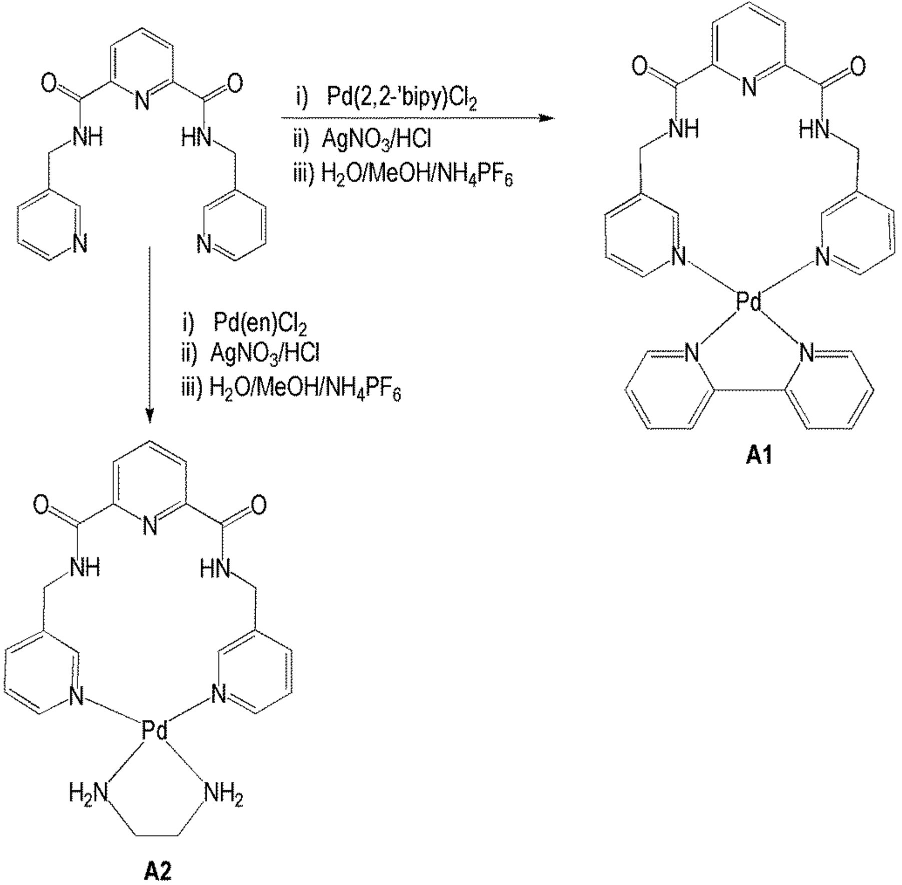
Unless otherwise stated, all chemicals were obtained from commercial sources and used as received. Dichloromethane was dried by standard literature procedures and distilled fresh from calcium hydride as required. Ligand *N,N'*-2,6-bis(3-pyridylmethyl)pyridine dicarboxamide (**L**) was prepared according to methods described in the literature. [21] The palladium precursors with ancillary blocking ligands, dichloropalladium(II) 2,2'-bipyridine [$PdCl_2$(2,2'-bipy)] and dichloropalladium(II) ethylenediamine [$PdCl_2$(en)] were prepared based on the literature procedures. [22]

Syntheses of metallo-macrocycles

[Pd(bipy)(L)](PF_6)$_2$ (A1). [$PdCl_2$(2,2'-bipy)] (0.114 g, 0.34 mmol) and $AgNO_3$ (0.112 g, 0.67 mmol) were dissolved in water (5 mL). A drop of concentrated HNO_3 was added and the mixture was heated at 100°C for 2 hrs. The resulting solid was removed by filtration and the filtrate was added to a stirred solution of **L** (0.116 g, 0.34 mmol) in methanol (25 mL). After stirring for 5 mins, ammonium hexafluorophosphate (0.217 g, 1.32 mmol) was added and the reaction was left to stir overnight. The precipitate obtained was collected, washed with water and dried under vacuum to give [Pd(bipy)(**L**)]$(PF_6)_2$ as a fine white solid (0.22 g, 77%). Mp 225-228°C. Anal. found: C, 40.38; H, 4.53; N 11.64. $PdC_{29}H_{24}N_7O_2P_2F_{12}$ requires C, 39.74; H, 4.70; N 11.20%; ^{1}H (300 MHz; DMSO-d_6) δ = 4.36 (2H, 2d, py*CH₂*NH), 5.32 (2H, m, py*CH₂*NH), 7.25 (2H, 2d, bipyH5), 7.65 (2H, 2d, bipyH4), 7.83 (2H, m, bipyH6), 8.27 (2H, m, pyH5'), 8.44 (2H, d, pyH4'), 8.71 (2H, m, pyH3, pyH5), 9.18 (1H, 2d, pyH4), 9.28 (4H, m, bipyH6, pyH6'), 9.76 (2H, 2d, pyH2') and 9.89 (1H, 2d, NH). Selected IR bands (KBr disk, cm^{-1}): 3385, 1663, 1537, 1444 and 830 cm^{-1}. *m/z* (ES-MS) 755.3 ({Pd(bipy)(**L**)]$(PF_6)\}^+$, MH$^+$, 10%).

[Pd(en)(L)]$(PF_6)_2\cdot H_2O\cdot 2CH_3OH$ (A2). [$PdCl_2$(en)] (0.171 g, 0.72 mmol) and $AgNO_3$ (0.245 g, 0.40 mmol) were dissolved in water (5 mL). A drop of concentrated HNO_3 was added and the mixture was heated at 100°C for 2 hrs. The resulting solid was filtered off and the filtrate added to a stirred solution of **L** (0.25 g, 0.72 mmol) in methanol (25 mL). After stirring for 5 mins, ammonium hexafluorophosphate (0.47 g, 2.8 mmol) was added and the reaction was left to stir overnight. The precipitate obtained was collected, washed with water and dried under vacuum to give [Pd(en)(**L**)]$(PF_6)_2\cdot H_2O\cdot 2CH_3OH$ as a grey solid (0.20 g, 46%). Mp 215-218°C. Anal.found: C, 31.26; H, 2.87; N 10.37. $PdC_{24}H_{34}N_7O_5P_2F_{12}$ requires C, 31.18; H, 3.99; N 11.07%; ^{1}H (300 MHz; DMSO-d_6) δ = 4.77 (4H, d, py*CH₂*NH), 5.26 (4H, m, CH_2*CH₂*NH_2), 7.64 (2H, m, pyH3', pyH5'), 8.08 (1H, d, pyH4'), 8.30 (2H, m, pyH3, pyH5), 8.86 (2H, d, pyH4), 8.89 (2H, m, pyH2', pyH6') and 9.76 (1H, 2d, NH). Selected IR bands (KBr disk, cm^{-1}): 3389, 1671, 1541, 1440 and 831 cm^{-1}. *m/z* (ES-MS) 513.2 ({[Pd(en)(**L**)]$(PF_6)^+\}$, MH$^+$, 10%).

Results and Discussion



Scheme 1. Preparation of complexes **A1** and **A2**

As mentioned earlier, reaction of **L** with [$PdCl_2$(2,2'-bipy)] and [$PdCl_2$(en)] gave rise to two mononuclear metallomacrocylic complexes, [Pd(2,2'-bipy)(**L**)](PF_6)$_2$ (**A1**) and [Pd(en)(**L**)](PF_6)$_2$·H_2O·2CH_3OH (**A2**), respectively. The palladium(II) complexes reported here were prepared based on literature procedures described for the formation of related palladium(II) supramolecular assemblies.[23-25] Ligand **L** was reacted with [$PdCl_2$(2,2'-bipy)], which has been pre-treated with silver nitrate to remove the chloride anions, in a 1:1 ligand to metal ratio. After stirring for 15 minutes the resulting complex was treated with ammonium hexafluorophosphate and left to stir overnight at room temperature to give a white powder of [Pd(2,2'-bipy)(**L**)](PF_6)$_2$ (**A1**) in 77% yield. In a similar manner, reaction of ligand **L** with pre-treated [$PdCl_2$(en)] gave complex [Pd(en)(**L**)](PF_6)$_2$·H_2O·2CH_3OH (**A2**) which was also obtained as a white solid in 72% yield (Scheme 1).

Electrospray ionisation mass spectrometry (ESI-MS) confirmed the formation of 1:1 discrete metallo-macrocycle complexes in solution for both **A1** and **A2**. The ESI-MS conducted in acetonitrile-methanol indicates a low intensity peak at *m/z* 755.3 corresponding to the [Pd(2,2'-bipy)(**L**)]$^+$ species. A peak at *m/z* 513.2 was observed for the [Pd(en)(**L**)]$^+$ species, also in a relatively low abundance. In the IR spectra, several characteristic strong bands of **L** were found at 3385, 1667 and 1537 cm^{-1} for complex **A1** and 3231, 1671 and 1541 cm^{-1} for complex **A2**. The N-H and C=N stretches of the ligand were shifted to the higher frequency due to the chelation of the ligand to the palladium centre. The ^{1}H NMR spectra of complexes **A1** and **A2** were consistent with a symmetrical compound, and consistent with the formula suggested by elemental analysis. In complex **A1**, the resonance at 9.89 ppm was assigned to the NH peak and the 2,2'-bipyridine protons have signals between 7.25-7.83 ppm. A peak at 4.36 ppm which appears as the expected doublet was assigned to the methylene protons. In the NMR spectrum of mononuclear **A2**, the resonance for NH amide appears slightly further upfield at 9.76 ppm, compared to complex **A1**. The pendant pyridine and pyridine core protons have signals between 7.64-8.89 ppm, while the methylene group has appears as a doublet at 4.77 ppm. A signal at 5.26 ppm corresponds to the methylene group (-CH_2-) and also corresponds to (NH_2) from ethylenediamine spacer. The aromatic regions of the ^{1}H NMR spectra of complexes **A1** and **A2** and ligand **L** are shown in Figure 1.

There are significant changes in the chemical shifts for the H2'/H6' of the pendant pyridine of **L** in both complexes ranging from 0.8-1, although these are significantly more pronounced for **A1** possessing the 2,2'-bipyridine ancillary ligand. An aspect of the shifts of these protons is due to the coordination of the pyridyl nitrogen atom to the palladium centre, but as demonstrated by more dramatic changes for **A1**, also due to the coordination bringing the pendant pyridyl ring into the deshielding region of the 2,2'-bipyridine ancillary ligand. To further examine the structure of these complexes in solution, both complexes were analyzed by 2D COSY and 2D NOESY techniques, in DMSO-d_6. The 2D COSY showed, as expected, a correlation between the protons at the methylene linker -CH_2- and the amide NH protons. The downfield peaks were assigned to the individual pyridyl rings from correlations in the COSY spectrum. More importantly, a through space interaction was obtained between the H6' protons of the pendant pyridyl ring of **L** and the H6' protons of the 2,2'-bipyridine co-ligand in complex **A1**. The same through space interaction was also observed in complex **A2**, between the H6' protons of the pendant pyridyl ring of **L** and the NH_2 protons of the ethylenediamine spacer (Figure 2).

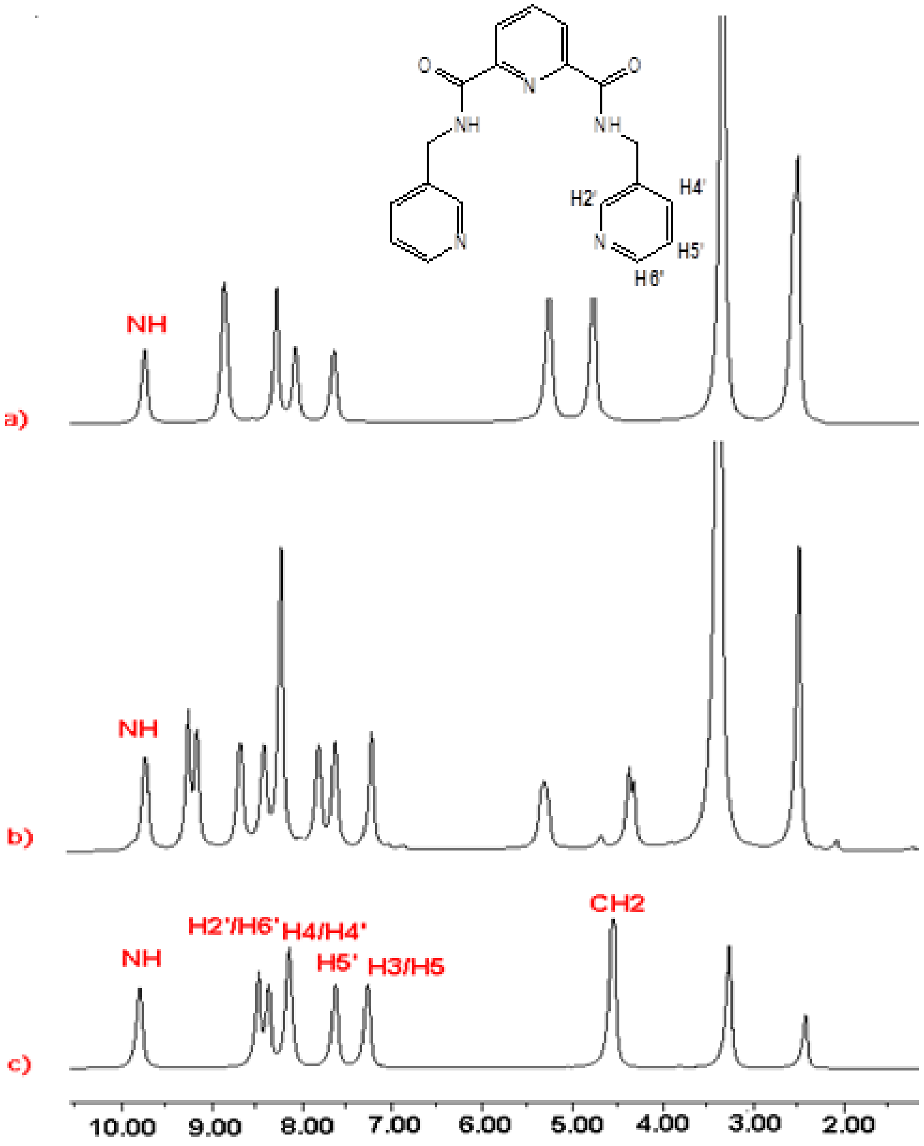
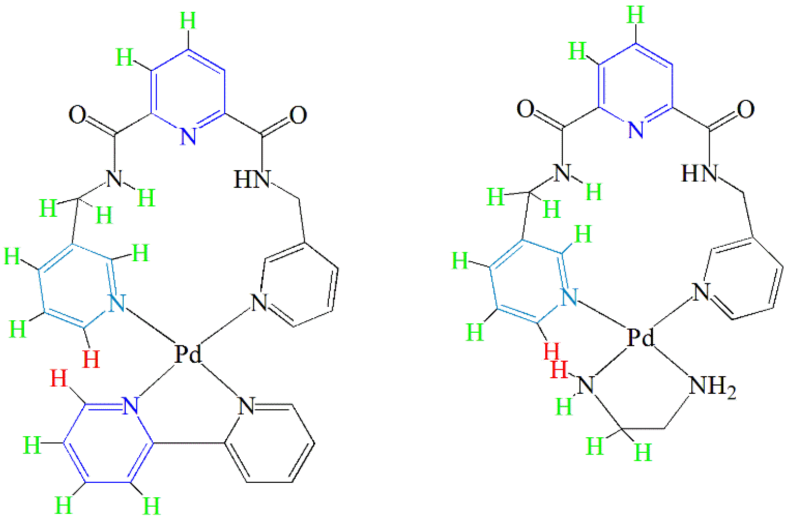


Figure 1. The aromatic region of the ^{1}H NMR spectrum of complex (a) [Pd(en)(**L**)]$(PF_6)_2 \cdot H_2O \cdot 2CH_3OH$ (b) [Pd(2,2'-bipy)(**L**)]$(PF_6)_2$, and (c) ligand **L** recorded in DMSO-d_6.



A1 **A2**

Figure 2. The protons correlations indicated by the $^1H^1H$ COSY and COSY correlations as well as 2D NOESY experiments. These molecules are symmetry, therefore only half of the molecules are highlighted for clarity.

DOSY NMR is used to further investigate the behaviour of these complexes in solution. DOSY NMR is commonly used to identify different compounds in a mixture based on the differing translational diffusion coefficients. This technique is useful to estimate the relative size of a molecule from a comparison of the diffusion rates. DOSY revealed that complex **A1** has a diffusion coefficient of $0.60 \pm 0.01 \times 10^{10}$ m^2/s. The diffusion coefficient of **A2** under the same condition was $0.62 \pm 0.02 \times 10^{10}$ m^2/s. The original ligand (**L**) has a diffusion coefficient of $0.98 \pm 0.02 \times 10^{10}$ m^2/s and the calculated ratio D_{A1}/D_L and D_{A2}/D_L for both mononuclear complexes are 0.60 and 0.63, respectively. Surprisingly, this value is lower from the theoretical ratio of 0.72 – 0.75 expected for a dimeric species of hard spheres [26- 27] and within the range of large species such as trimer of hard spheres. [26] This surprisingly slow diffusion rate may be a factor of the vastly different shapes of the unreacted ligand and the bowl-shaped mononuclear palladium complexes. Furthermore, complexation of the anions might increase the hydrodynamic radii of the complex, hence slowing its diffusion rate further. Nonetheless, the results showed that the relative sizes of complexes **A1** and **A2** are almost similar. As an attempt to provide further understanding of the structure of these compounds, **A1** and **A2** were dissolved in a mixture of acetonitrile-methanol and left to evaporate at room temperature. After several weeks, complex **A2** crystallized in 50% as plate-like colourless crystals which were suitable for X-ray crystallography. Unfortunately, crystals of **A1** were not obtained by any recrystallization approaches. Several attempts in recrystallizing **A1** using different combination of solvents including slow diffusion by methanol in dimethylformamide gave sticky oils as final product which cannot be characterized by any methods. Incorporation of inorganic solvents led to formation of **A1** in the solid form. The difficulty in obtaining the crystals of **A1** might be attributed by bulk size of this compound that limits its solubility in many solvents.

Crystal structure of A2

Complex **A2** crystallizes in the monoclinic space group $P2_1/n$ with one complete molecule of **L** chelating the palladium(II) ethylenediamine centre, two hexafluorophosphate anions and two methanol molecules and one water in the asymmetric unit (Figure 3).

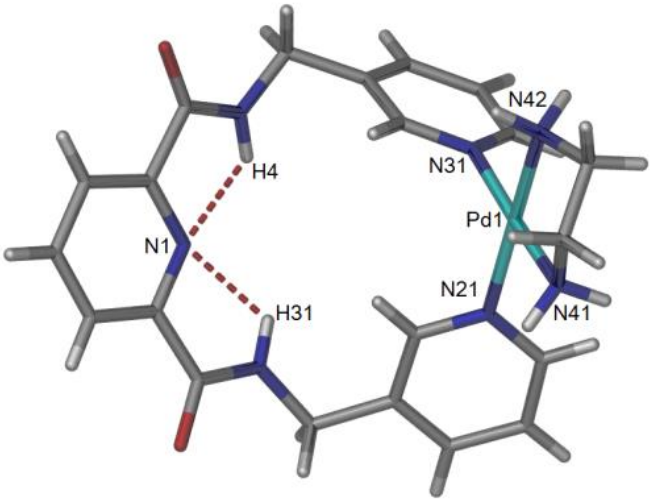


Figure 3. A perspective view of the asymmetric unit of complex **A2** with hexafluorophosphate anions, methanol and water solvate molecules omitted for clarity. Selected bond lengths (Å): N(21)-Pd(1) 2.024(6), N(31)-Pd(1) 2.028(6), N(41)-Pd(1) 2.017(3) ,N(42)-Pd(1) 2.046(5), N(31)-Pd(1)-N(21) 90.42(2), N(31)-Pd(1)-N(40) 92.94(2), N(41)-Pd(1)-N(42) 84.51(2) and N(21)-Pd(1)-N(41) 91.93(2).

Table 1. The distances of the weak interaction in complex **A2**.

Atoms involve in weak bonding		**Distance/Bond length (Å)**
C-H···F	C···F	3.297
	F···H	2.501
N-H···F	N···F	(a)3.113, (b)3.124
	F···H	(a)2.379, (b)2.342
Centroid···F		3.197

The palladium atom adopts a distorted square planar geometry with typical Pd-N bond lengths (2.024(6)– 2.045(6) Å) and angles (84.51(2) – 92.94(3)°). Similar distances and angles are observed in related mononuclear complexes with palladium. [23] The palladium atom is coordinated by two nitrogen donors from the pyridyl groups and two nitrogen atoms from the ethylenediamine ancillary chelating ligand. In this complex, ligand **L** maintains the U-shape conformation with the amide hydrogen bond donors (N1···H4 = 2.239 Å) and (N1···H31 = 2.268 Å) controlling the conformation of **L**. In this complex, twisting of the ligand enables the macrocycle to form a bowl-like structure with one hexafluorophosphate anion encapsulated at the centre of the macrocycle (Figure 4(a) and Figure 4(b)). The 3-pyridyl rings twist out of the plane of the core of **L**, and coordinate the palladium centre to form the metallo-macrocycles (torsion angles for C11-N13-C14-C23 are 110.42 – 112.17°). It is well known that the use of flexible ligands provide access to supramolecular clefts or clips [28] or shallow bowl-like structures. [30-35] The structure of this complex is also similar to other palladium(II) complexes obtained with angular bispyridyl amide ligands.[10] The encapsulation of the hexafluorophosphate (PF_6) anion within the cavity of **A2** is stabilized by weak C-H···F hydrogen bonding with ligand **L**; the C···F distance is 3.297 Å, while the F···H distance is 2.501 Å. This is shorter than the sum of van der Waals radii of 2.67 Å. The hexafluorophosphate anions also form hydrogen bonds with the co-ligand, ethylenediamine (N-H···F, d = 2.379, D = 3.113 Å). Finally, the encapsulation is stabilized by anion-π contacts between the anion and the central pyridine ring. The shortest contact between the centroid of the pyridine ring is 3.197 Å. The summary of the weak interactions is listed in Table 1.This is comparable to such anion-π interactions previously reported in the literature for solid-state structures. [36, 37] The second hexafluorophosphate anion is also hydrogen bonded to the complex and forms intermolecular hydrogen bonding interactions involving the pre-organized NH amide donors (d = 2.342 and 3.124 Å). The bond lengths and angles are in normal ranges [38] and comparable to those reported in previous studies. [12-15]

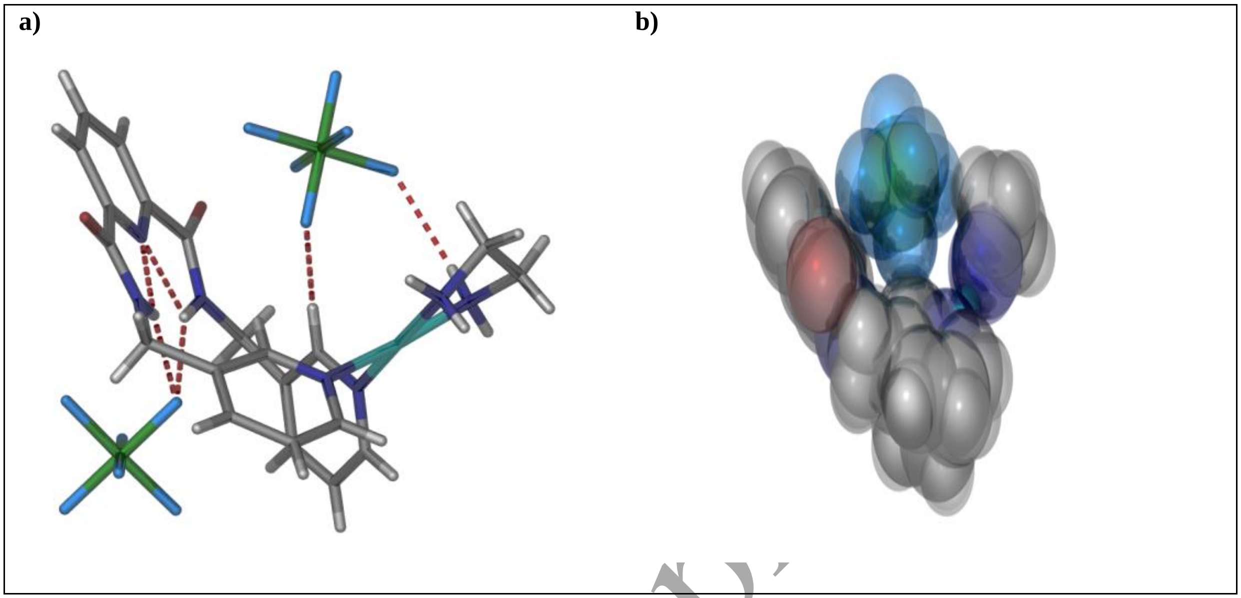


Figure 4. A perspective view of (a) complex **A2** showing one PF_6^- located inside the cavity of the macrocycle and bound through hydrogen bonding interactions and anion-π interactions. Weak intramolecular and intermolecular hydrogen bonding interactions between the pre-organised amide NH and the PF_6^- anions are demonstrated. (b) A close interaction between the anion and the macrocycle.

Conclusion

In conclusion, two mononuclear palladium(II) metallo-macrocyles with potential to bind anions have been successfully synthesized and characterized *via* several spectroscopies technique. The flexibility of the ligand allows complex **A2** to fold into a bowl-shaped structure to get closed to the hexafluorophosphate anion that encapsulated at the centre of the macrocycle. X-ray crystallography has revealed that the PF_6^- anions interacted with the macrocyclic complex through weak hydrogen bonding and anion-π interactions. Complex **A1** is expected to have similar structure with complex **A2** (bowl shaped) as similar hydrogen bond interactions were indicated by 2D COSY and 2D NOESY NMR. Further investigation on the potential of this type of metallo-macrocycles to interact with other anions such as nitrate, perchlorate and chromate will be attempted in line with our target to utilize palladium(II) supramolecular assemblies as universal anion receptors.

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