

Characterizations and X-ray Crystal Structure of Asymmetrical 2,4,9,11-Tetramethyl-1,5,8,12-monobenzotetraazacyclo[14]annulene Palladium(II) Complex

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It is reported that symmetrical dibenzotetraazacyclo[14]annulene are generally complexed with a variety of metals such as nickel, copper and cobalt.¹⁻⁷ The studies of the metal complexes of tetraazaannulene, which have been well known to possess chemical and thermal stability, have been of considerable attention because of their utilities as electrocatalysts or model compounds in biological system.⁸⁻¹⁴ Tetraazaannulenes as ligands prefer to coordinate with a metal ion in a square-planar fashion like porphyrines or phthalocyanines. Especially, palladium coordination complexes with macrocycle ligands such as tetraazaannulene or porphyrin typically prefer a square-planar arrangement as the most stable structure and are very resistive to chemical demetallation due to the stability of its square-planarity.¹⁵⁻¹⁷ The first X-ray structure of symmetrical tetraaza[14]annulene palladium(II) complex is reported by Tsutsui, M. *et al.* in 1979.¹⁸ The complexes reported in asymmetrical monobenzotetraaza[14]annulene are mostly to include nickel(II) ion.^{19,20} On the other hand, the palladium complex has scarcely been reported because it is not easy to prepare an asymmetrical free-based ligand in comparison to symmetrical free-based ligand. Herein, we synthesized and characterized a free-based asymmetrical 2,4,9,11-tetramethyl-1,5,8,12-monobenzotetraazacyclo[14]annulene (L) and its palladium complex ([PdL]) and determined the structure of the [PdL] by X-ray diffraction study.

Experimental Section

Materials. Ni(OAc)₂·4H₂O, 1,2-phenylenediamine, 1,2-diaminoethane, Pd(OAc)₂, NaCN and 2,4-pentandione were purchased from Aldrich and Fluka. The solvents such as CH₃CN, CH₃OH, CH₂CH₂OH, CH₂Cl₂ were refluxed over calcium hydride under nitrogen, and checked for purities by GC just before use. Dimethylsulfoxide (DMSO) was purchased from Merck and used without further more purification. Tetraethylammonium perchlorate (TEAP) used as supporting electrolyte was prepared and purified by the method described by Kolthoff and Coetzee.²¹

Measurements. Elemental analyses (C, H, N) of the compounds prepared were carried out on a Carlo-Ebra. EA 1108 instrument. Infrared spectra were recorded on a Matteson Instruments, Inc. Galaxy 7020 A using KBr Pellets. ¹H-NMR (300 MHz) spectra were recorded on a Bruker instrument at room temperature and chemical shifts in CDCl₃ were given in ppm relative to tetramethylsilane as internal reference. Electronic absorption spectra were obtained on a Shimadzu UV-265 spectrophotometer.

Cyclic voltammetry was performed using a Bioanalytical System (BAS) CV-50W electrochemical analyzer and C2 cell stand at room temperature. The three electrodes system for the electrochemical measurements composed of the glassy carbon electrode as a working electrode, and Ag/Ag⁻ (0.01 M AgNO₃ in 0.1 M TEAP DMSO solution) as a reference electrode, and a platinum wire as an auxiliary electrode was used

Synthesis: 2,4,9,11-Tetramethyl-1,5,8,12-monobenzotetraazacyclo[14]annulene (L). This ligand was prepared by modifying L'Éplattenier and Pugin's method.²² At first the asymmetrical 2,4,9,11-tetramethyl-1,5,8,12-monobenzotetraaza-cyclo[14]annulene nickel(II) as starting compound was prepared by the method reported in the literature.^{23,24} The complex (5.28 g, 0.015 mol) was dissolved in absolute ethanol (50 mL) and was treated excess anhydrous hydrochloric acid until the blue colored ligand salt precipitate. The reaction mixture was further stirred at room temperature for 18 h. The solid was filtered, dissolved in water (300 mL) and neutralized by addition of solid sodium cyanide. The yellow precipitate was recovered, washed with water, dried in *vacuo*. The red single crystal could be obtained by recrystallizing from a mixture (1 : 1) of dichloromethane and methyl alcohol. Yield 1.11 g (25%). Anal. Calcd. for C₁₈H₂₄N₄: C, 72.94; H, 8.16; N, 18.90%. Found: C, 72.78; H, 8.22; N, 18.93%. IR (KBr disc, cm⁻¹): ν (C=C), 1502; ν (C=N), 1562; ν (C₆H₆), 746. UV-vis: λ_{max} (nm) and ϵ_{max} (M⁻¹cm⁻¹) in CHCl₃ 322 and 36000. ¹H NMR (CDCl₃): 1.972, 2.101 (s) (methyl); 4.757(s) (methine); 3.443(s) (ethylene); 6.945 (m) (aromatic); 11.873 (br) (N-H).

2,4,9,11-Tetramethyl-1,5,8,12-monobenzotetraazacyclo[14]annulene palladium(II) ([PdL]). Pd(OAc)₂ (0.224 g, 0.001 mol) and free based ligand (L: 0.296 g, 0.001 mol) was

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dissolved in acetonitrile (80 mL). The mixture was heated under reflux for 2 h with stirring and bubbled nitrogen gas for protecting from moisture. The reaction mixture was left to stand in refrigerator for 12 h. The solid was filtered and washed with acetonitrile. The product was chromatographed on aluminum oxide and eluted with chloroform. The yellow effluent was collected, evaporated to dryness in *vacuo* and dried. The dark brown crystal was obtained by recrystallizing from a mixture of dichloromethane and methyl alcohol (1 : 1). When the powder was yellow color but the crystal was dark brown. Yield 0.159 g (40%). Anal. Calcd. for $C_{18}H_{20}PdN_4$: C, 54.17; H, 5.02; N, 14.11%; Found: C, 53.79; H, 5.64; N, 14.11%. IR (KBr disc, cm^{-1}): ν (C=C), 1514; ν (C=N), 1569; ν (C₆H₆), 744. UV-vis: λ_{max} (nm) and ϵ_{max} ($M^{-1} cm^{-1}$) in $CHCl_3$ 374 and 19000, 432 and 11000. ¹H NMR ($CDCl_3$): 2.187, 2.569 (s) (methyl); 4.998 (s) (methine); 3.773 (s) (ethylene); 6.820-7.514 (m) (aromatic).

X-ray crystallographic analysis: Preliminary examination and data collection for crystal of palladium(II) complex were performed with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) on an Enraf-Nonius CAD4 computer controlled *k*-axis diffracto-

Table 1. Crystal data and structure refinement for palladium(II) complex ([PdL])

Empirical formula	C ₁₈ H ₂₀ N ₄ Pd
Formula weight	398.78
Temperature	173(2) K
Wavelength	0.71073 \AA
Crystal system	Orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
Unit cell dimensions	a = 8.1003(12) \AA $\alpha = 90^\circ$ b = 8.2553(13) \AA $\beta = 90^\circ$ c = 24.416(4) \AA $\gamma = 90^\circ$
Volume	1632.7(4) \AA^3
Z	4
Density (calculated)	1.622 Mg/m ³
Absorption coefficient	1.141 mm ⁻¹
F(000)	808
Crystal size	0.38 × 0.28 × 0.25 mm ³
Theta range for data collection	1.67 to 28.32°
Index ranges	-10 ≤ h ≤ 10 -10 ≤ k ≤ 10 -32 ≤ l ≤ 23
Reflections collected	9553
Independent reflections	3837 [R(int) = 0.0283]
Completeness to theta = 28.32°	96.3%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7635 and 0.6710
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3837 / 0 / 212
Goodness-of-fit on F ²	1.096
Final R indices [I > 2sigma(I)]	R1 = 0.0218, wR2 = 0.0571
R indices (all data)	R1 = 0.0228, wR2 = 0.0576
Absolute structure parameter	0.03(3)
Largest diff. peak and hole	0.583 and -0.755 e. \AA^{-3}

Table 2. Selected bond distances [\AA] and angles [$^\circ$] for palladium(II) complex ([PdL])

Pd-N(1)	1.977(2)	Pd-N(2)	1.978(2)
Pd-N(3)	1.966(2)	Pd-N(4)	1.957(2)
N(1)-C(1)	1.409(3)	N(1)-C(16)	1.343(3)
N(2)-C(2)	1.410(3)	N(2)-C(7)	1.341(3)
N(3)-C(9)	1.307(3)	N(3)-C(12)	1.461(4)
N(4)-C(13)	1.452(4)	N(4)-C(14)	1.391(4)
C(1)-C(2)	1.441(3)	C(1)-C(6)	1.393(3)
C(7)-C(8)	1.393(4)	C(7)-C(10)	1.517(3)
C(8)-C(9)	1.419(4)	C(9)-C(11)	1.508(4)
C(12)-C(13)	1.446(5)		
N(1)-Pd(1)-N(2)	83.75(8)	N(4)-Pd(1)-N(1)	96.21(9)
N(4)-Pd(1)-N(3)	83.78(9)	N(4)-Pd(1)-N(2)	177.61(9)
N(3)-Pd(1)-N(1)	178.11(9)	N(3)-Pd(1)-N(2)	96.19(9)
C(9)-N(3)-C(12)	122.5(2)	C(7)-N(2)-C(2)	127.3(2)
C(9)-N(3)-Pd(1)	123.43(18)	C(7)-N(2)-Pd(1)	120.62(17)
C(12)-N(3)-Pd(1)	113.56(19)	C(2)-N(2)-Pd(1)	111.49(15)
N(2)-C(2)-C(1)	115.3(2)	N(2)-C(7)-C(8)	123.3(2)
N(2)-C(7)-C(10)	121.9(2)	N(3)-C(9)-C(8)	122.4(2)
C(8)-C(7)-C(10)	114.8(2)	N(3)-C(9)-C(11)	120.8(2)
C(7)-C(8)-C(9)	130.4(2)	C(12)-C(13)-N(4)	113.7(2)
C(8)-C(9)-C(11)	116.7(2)		

meter equipped with a graphite crystal, incident-beam monochromator. Cell constants and orientation matrices for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections. The data were collected for Lorentz-polarization and absorption corrections were applied to the data. The structure was solved by direct methods using SHELXS-86 and refined by full-matrix least-squares calculations with SHELX-97.^{25,26} The final cycle of the refinement converged with R = 0.0218 and wR = 0.0571. Crystal data, details of the data collection, and refinement parameters were listed in Table 1. The selected bond distances and angles were presented in Table 2.

Results and Discussion

The UV-visible spectra of the free ligand **L** and the complex [PdL] newly prepared were illustrated in Figure 1. The spectrum of the **L** showed only one peak at 322 nm ($\epsilon_{max} = 36000 M^{-1} cm^{-1}$) attributed to $\pi \rightarrow \pi^*$ transitions, while that of the [PdL] exhibited a band of ligand based at 374 ($\epsilon_{max} = 19000 M^{-1} cm^{-1}$) and a band at 432 nm ($\epsilon_{max} = 11000 M^{-1} cm^{-1}$) in $CHCl_3$. The latter band may be attributed to ligand to metal charge transfer (LMCT) from the highest occupied ligand molecular orbital to the lowest empty *d*-orbital of palladium. The LMCT band of the asymmetrical complex [PdL] shifted to higher energy than asymmetrical monobenzotetraazacyclo[14]annulene nickel(II) complex ($\lambda_{max} = 547 \text{ nm}$ and $\epsilon_{max} = 3000 M^{-1} cm^{-1}$) owing to the extended interaction by the larger *d*-orbital of palladium.¹³ In the ¹H-NMR data, the characteristic peak (*N-H*) of free-based ligand appeared at 11.873 (s) ppm, while disappearing in the palladium(II) complex.

The cyclic voltammograms of the ligand **L** and the

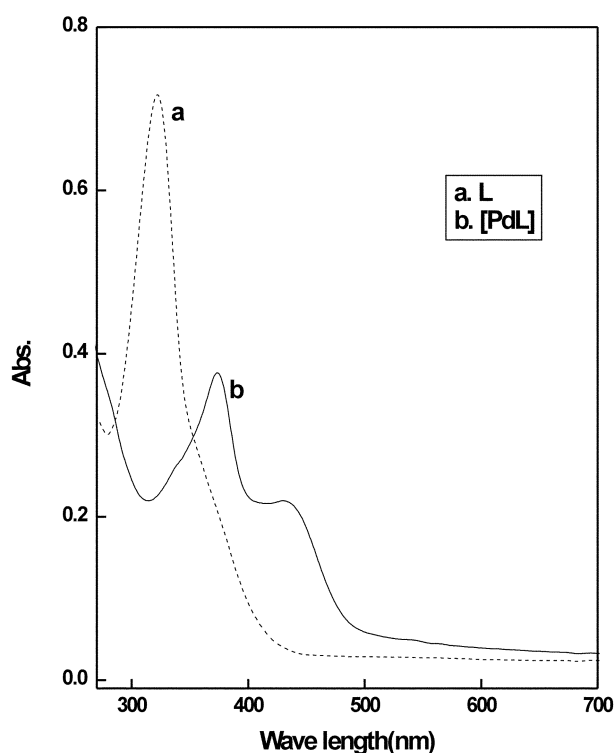


Figure 1. Electronic absorption spectra of free ligand and palladium(II) complex in chloroform solution at room temperature.

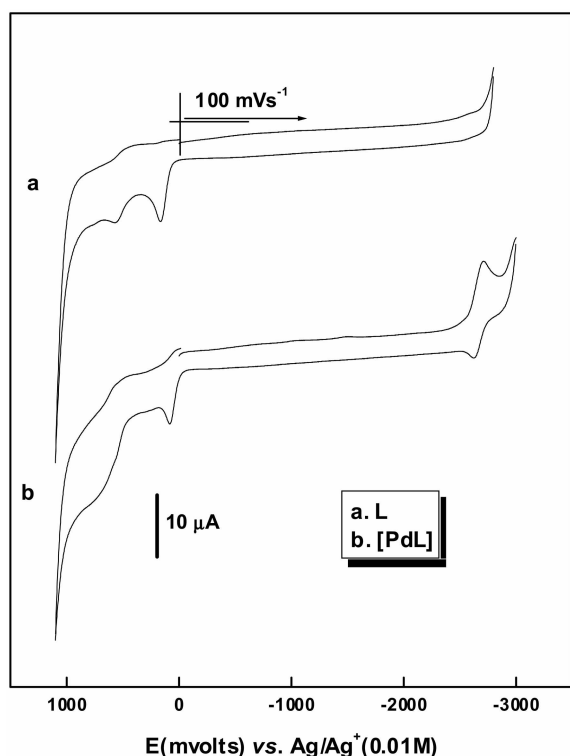


Figure 2. Cyclic voltammograms of free ligand and palladium(II) complex in a 0.1 M TEAP-DMSO solution at room temperature.

complex **[PdL]** measured in 0.1 M TEAP-DMSO solutions vs Ag/Ag^+ (0.01 M) at 25 °C and scan rates of 100 mVs^{-1} were shown in Figure 2. The **L** has only two irreversible

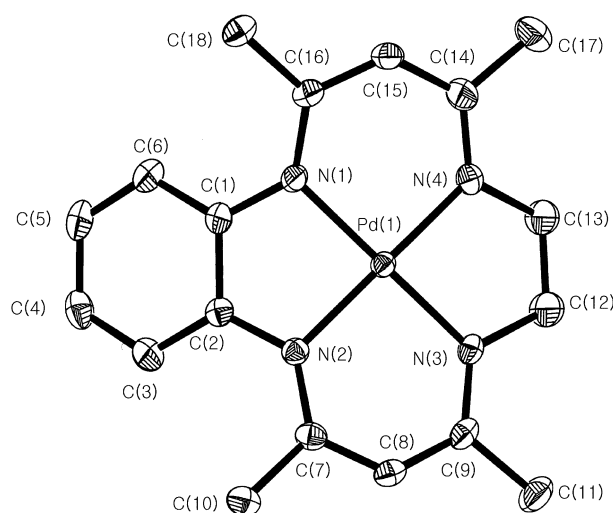


Figure 3. The molecular structure of palladium(II) complex.

oxidation peaks at +0.170 and -0.580 V . The **[PdL]** has two irreversible oxidation peaks by one electron at +0.090 and -0.700 V , respectively, and one quasi-reversible reduction peak by one electron of palladium-based ($\text{Pd}^{2+} \rightarrow \text{Pd}^+$) at -2.710 V . Such assignments of redox waves are supported by similar observation with asymmetrical monobenzotetraazacyclo[14]annulene nickel(II) complex.²⁷

The molecular structure of the complex **[PdL]** was drawn in Figure 3. Crystal data and refinement parameters and the selected bond distances and angles were presented in Tables 1 and 2, respectively. The average of four Pd-N bond distances was 1.970 \AA that is longer than the corresponding Ni-N distances (1.870 \AA) for symmetrical nickel(II) complex²⁸ but shorter than Pd-N distances (1.996 \AA) for symmetrical palladium complex¹⁸ owing to different basicity for phenylenediamine and ethylenediamine. Such difference of bond distances might be attributed to the larger ionic radius of palladium. Also, the distances of N-C on the side of six-membered rings were 1.343 \AA for N(1)-C(16), 1.341 \AA for N(2)-C(7), 1.307 \AA for N(3)-C(9) and 1.391 \AA for N(4)-C(14), while for five-membered rings they were totally longer (1.409 \AA for N(1)-C(1), 1.410 \AA for N(2)-C(2), 1.461 \AA for N(3)-C(12) and 1.452 \AA for N(4)-C(13)). The average C-C distances in the six-membered chelate rings were 1.408 \AA close to those of benzene (1.40 \AA), reflecting some aromaticity that all π -electrons are somehow delocalized in the macrocycle ring. The average angles of N-Pd-N of five and six member rings were 83.76 and 96.20° , and N(3)-Pd-N(1) and N(4)-Pd-N(2) were 178.11 and 177.61° , respectively, indicating the geometry close to a square planar a little bit distorted. The coordination environment around the central palladium(II) atom showed a square planar geometry with four Pd-N bonds, which is very similar to that of symmetrical dibenzotetraazacyclo[14]annulene palladium(II) complex.

Supplementary material. Crystallographic data for the structural analysis have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number CCDC 222447. Copies of this

information can be obtained free of charge via E-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>. Tel: +44-1233-336031; Fax: +44-1223-336033.

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