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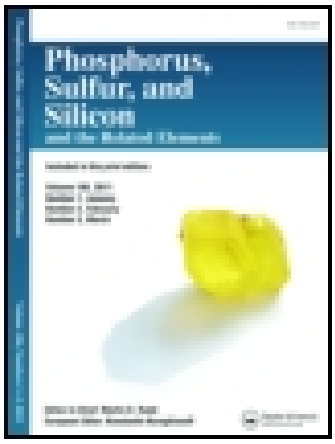

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Palladium(II) Mixed-Ligand Complexes Containing 2,2'-Bipyridine Derivaties and 4-Toluenesulfonyl-l-Serine: Synthesis, Characterizationand Crystal Structure Determination

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PALLADIUM(II) MIXED-LIGAND COMPLEXES CONTAINING 2,2'-BIPYRIDINE DERIVATIES AND 4-TOLUENESULFONYL-L-SERINE: SYNTHESIS, CHARACTERIZATIONAND CRYSTAL STRUCTURE DETERMINATION

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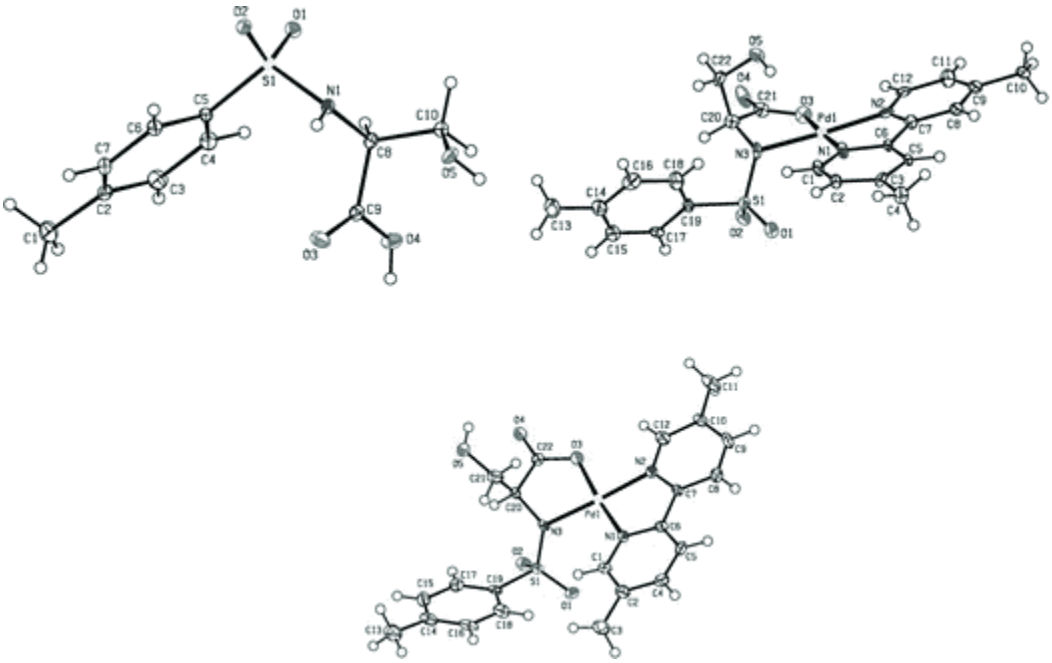
Abstract

The 4-toluenesulfonyl-L-serine ligand (**1**), (tsserH_2), was prepared from the reaction of L-serine and 4-toluenesulfonyl chloride in sodium hydroxide solution 1M. The complexes [Pd(4,4'-dmbipy)(tsser)] (**2**) and [Pd(5,5'-dmbipy)(tsser)].0.5CH_3CN (**3**) (4,4'-dmbipy is 4,4'-dimethyl-2,2'-bipyridine and 5,5'-dmbipy is 5,5'-dimethyl-2,2'-bipyridine) were also prepared from the reaction of $PdCl_2$ and 2,2'-bipyridine derivatives with 4-toluenesulfonyl-L-serine ligand in

mixture of CH_3CN/CH_3OH (3:1) and in presence of sodium hydroxide solution 0.5M. These compounds were characterized by elemental analysis, IR, ^1H NMR and UV–Vis spectroscopy and their structures were studied by single-crystal X-ray diffraction method. The X-ray structure determinations show that in the both complexes, the Pd^{II} atoms are four-coordinated in a distorted square-planar configuration by two N atoms from a bidentate bipyridine ligand and one N atom and one O atom from a bidentate $tsser^{2-}$ ligand.



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Keywords Crystal structure; palladium(II) complexes; 4-toluenesulfonyl-L-serine; 4,4'-dimethyl-2,2'-bipyridine; 5,5'-dimethyl-2,2'-bipyridine

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1. Introduction

Palladium(II) complexes are well-known to show interesting applications in catalysis,[1-4] optics[5-7] and possess antibacterial and antifungal properties.[8-10] Palladium(II) complexes have been also investigated for developing the new antitumor agents because palladium(II) has a similar coordination mode and chemical properties to platinum(II) complexes.[11-17] There are only eight palladium(II) mixed-ligand complexes with formula, [Pd(L)(amino acid)], such as that of [pd(bipy)(Gly)]Cl.4H_2O, [pd(phen)(Gly)]Cl.4H_2O and [pd(bpa)(Gly)]Cl.3H_2O (Gly is glycine, bipy is 2,2'-bipyridine, phen is 1, 10-phenanthroline and bpa is 2,2'-bipyridylamine),[17] [pd(1,3-dap)(tsser)] (1,3-dap is 1,3-diaminopropane),[18] [pd(1,3-dap)(tsval)] (tsvalH_2 is 4-toluenesulfonyl-L-valine),[19] [pd(tsval)(phen)].2H_2O,[20] [pd(dab)(tsala)] (dab is 1,4-diaminobutane and tsalaH_2 is 4-toluenesulfonyl-L-alanine),[21] [pd(en)(tsser)] (en is ethylene diamine),[22] have been synthesized and full characterized by technicals spectroscopy and their structures were studied by single-crystal X-ray diffraction method. Also, all of these palladium(II) mixed-ligand complexes have shown significant cytotoxic activities against several human tumor cell lines. We report herein the synthesis, characterization and crystal structure of the 4-toluenesulfonyl-L-serine ligand (**1**) and two [Pd(4,4'-dmbipy)(tsser)] (**2**) and [Pd(5,5'-dmbipy)(tsser)].0.5CH_3CN (**3**) complexes.

2. Results and discussion

2.1. Synthesis of **1**, **2** and **3**

4-Toluenesulfonyl-L-serine (**1**) was synthesized according to the reported procedure.[18] Suitable crystals of **1** for X-ray diffraction study were grown by slow evaporation of a 1:1 ratio

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of CH_3CN/CH_3OH solution at room temperature over one week. Compounds **2** and **3** were also obtained from the reaction one equivalent of $PdCl_2$ and one equivalent of N-N ligand (N-N is 4,4'-dimethyl-2,2'-bipyridine in **2** and 5,5'-dimethyl-2,2'-bipyridine in **3**) with one equivalent of 4-toluenesulfonyl-L-serine ligand in mixture of CH_3CN/CH_3OH (3:1) and in presence of sodium hydroxide solution 0.5M. Suitable crystals of **2** and **3** for X-ray diffraction study were grown by slow evaporation of its solution at room temperature over one week. The synthetic routes of these compounds are shown in Scheme 1.

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2.2. Description of the molecular structure of **1**, **2** and **3**

Crystallographic data for **1**, **2** and **3** are given in Table 1 and selected bond lengths and angles are presented in Table 2. The ORTEP view with the numbering scheme for **1** is shown in Figure 1. This compound crystallized in orthorhombic $P2_12_12_1$ space group. As shown in Figure 1, the carboxylic group and *p*-toluene ring are in the same side of molecular structure [torsion angle: C5-S1-N1-C8 = 75.48(18)°]. In this compound, the bond lengths and angles are within normal ranges. [23]

In the crystal structure of compound **1**, Figure S1 (Supplemental Materials), there is no π-π interaction between the phenyl rings and intermolecular O-H···O, N-H···O and C-H···O hydrogen bonds (Table S 1 Supplemental Materials) are effective in the stabilization of the crystal structure and the formation of the 3D supramolecular compound.

[Insert Figure 1]

[Insert Table 1]

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The ORTEP view with the numbering scheme for complex **2**, [Pd(4,4'-dmbipy)(tsser)], is shown in Figure 2. As shown in Figure 2, each palladium(II) cation is four-coordinated in a distorted square-planar configuration by two N atoms from a bidentate 4,4'-dmbipy ligand and one N atom and one O atom from a bidentate $tsser^{2-}$ anion. The Pd-N_{bipy} bond lengths are 1.989(13) and 2.021(14)Å, Pd-N_{tsser} bond length is 2.014(12)Å and Pd-O bond length is 2.007(10)Å (Table 2). The Pd-N and Pd-O bond distances are within the ranges of those for other analogical palladium(II) complexes.[18-22] The N1-Pd-N2, N1-Pd-N3, N2-Pd-O3, and N3-Pd-O3 bond angles are 81.1(5), 99.5(5), 96.6(5), and 82.8(5)°, respectively (Table 2). The angle between planar N1-Pd1-N2 and planar O1-Pd1-N3 is 2.68° which indicates that the Pd1-O3-N3-N1-N2 plane is slightly distorted. Also, the pyridine rings are slightly distorted from planarity. The mean planes of rings A (N1/C1-C3/C5-C6), B (N2/C7-C9/C11-C12) and C (Pd1/N1/C6-C7/N2) make the following dihedral angles with each other: A/B = 7.00, A/C = 5.08 and B/C = 2.56°.

[Insert Table 2]

[Insert Figure 2]

In the crystal structure of **2**, Figure S 2 (Supplemental Materials), there is no π···π interaction between the pyridine and phenyl rings, and only intermolecular O-H···O and C-H···O hydrogen bonds (Table S 1) are effective in the stabilization of the crystal structure and formation of the 3-D supramolecular assembly.

The crystal structure of **3**, [Pd(5,5'-dmbipy)(tsser)].0.5CH_3CN, is given in Figure 3. As it is depicted in this Figure, the asymmetric unit of **3** contains one independent [Pd(5,5'-dmbipy)(tsser)] complex and half no coordinated CH_3CN molecule. In this complex,

palladium(II) cation is four-coordinated in a distorted square-planar configuration by two N atoms from a bidentate 5,5'-dmbipy ligand and one N atom and one O atom from a bidentate $tsser^{2-}$ anion. The Pd-N_{bipy} bond lengths are 2.000(4) and 2.002(4)Å, Pd-N_{tsser} bond length is 2.020(4)Å and Pd-O bond length is 1.992(4)Å (Table 2). The Pd-N and Pd-O bond distances are within the ranges of those for other analogical palladium(II) complexes. [18-22] The N1-Pd-N2, N1-Pd-N3, N2-Pd-O3, and N3-Pd-O3 bond angles are 80.58(17), 102.39(19), 94.38(18), and 82.61(17)°, respectively (Table 2). The angle between planar N1-Pd1-N2 and planar O1-Pd1-N3 is 3.55° which indicates that the Pd1-O3-N3-N1-N2 plane is slightly distorted. Also, the pyridine rings are slightly distorted from planarity. The mean planes of rings A (N1/C1-C2/C4-C6), B (N2/C7-C10/C12) and C (Pd1/N1/C6-C7/N2) make the following dihedral angles with each other: A/B = 5.78, A/C = 3.53 and B/C = 3.24°.

[Insert Figure 3]

In the crystal structures of complex **3**, Figure S 3, it seems that the main factors controlling the packing of the structure are intermolecular O-H···O, C-H···O and C-H···N hydrogen bonds (Table S 1) and π-π interactions between the pyridine and phenyl rings, $Cg3\cdots Cg4^{i}$ and $Cg3\cdots Cg5^{ii}$ [symmetry codes: (i) -x,2-y,z, (ii) -1/2+x,3/2-y,-z, where Cg3, Cg4 and Cg5 are centroids of the rings (N1/C1-C2/C4-C6), (N2/C7-C10/C12) and (C14-C19), with centroid-centroid distances of 3.816(3) and 3.901(3)Å, respectively].

2.3. Spectroscopic characterization of **1**, **2** and **3**

IR absorptions of **1**, **2** and **3** are listed in experimental section. The vibrational bands present at 3410 and 3277 cm^{-1} are assigned to $\nu(O\text{-}H)_{COOH}$ and ν(N-H), respectively for **1**. These bands disappear for the complexes of **2** and **3**, showing that the 4-toluenesulfonyl-L-serine ligand has

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been deprotonated. [18-21] The weak absorption bands present in the region 3051 to 2921 cm^{-1} are due to the C-H stretching of phenyl and pyridine rings and methyl groups. [24] In addition, the weak band at 2306 cm^{-1} in the IR spectrum of **3** has been assigned to ν(C≡N). [25] The strong band at 1732 cm^{-1} in the IR spectrum of **1** has been assigned to ν(CO). This band for the free ligand is shifted to lower frequencies upon coordination in **2** and **3**. The strong bands at 1627 and 1641 cm^{-1} are assigned to ν_{as}(COO) and the strong bands at 1375 and 1362 cm^{-1} are assigned to ν_{s}(COO) for complexes of **2** and **3**, respectively. The frequency difference Δν [$\Delta\nu = \nu_{as}(COO)-\nu_{s}(COO)$] is correlated with the coordination mode of a carboxylate ligand. The Δν differences are 252 and 279 cm^{-1} for compounds **2** and **3** respectively, which are greater than those of sodium acetate (164 cm^{-1}), as anticipated for a monodentate mode of the carboxylate ligand. [25-27] New bands present in the 260-434 regions are assigned to Pd-N_{bipy}, Pd-N_{tsser} and Pd-O_{tsser} stretching vibrations. [25, 28-31]

The UV–Vis spectra of dimethyl sulfoxid solutions of title compounds have a broad band in the region of 258-274 nm, assigned to the ligand π-π* transition. [19-21, 32] There is also a broad band at 304-322 nm for **2** and **3** assigned to the metal-to-ligand charge transfer (MLCT). [19-21]

The ^{1}H NMR spectra of title compounds in DMSO-d_6 solution are given in Figure 4. As depicted, the ^{1}H NMR spectrum of **1** exhibited a broad singlet at 12.45 ppm for the –COOH group and a doublet at 7.91ppm for the –NH group. These signals are absent in the spectra of compounds **2** and **3**, indicating the removal of the –COOH and –NH protons and the formation of Pd-O and Pd-N bonds. As shown in Figures 3 and 5, the X-ray structures of compounds **2** and **3** show that the half of bipyridine ligands lies down in the diamagnetic protection zone of the phenyl aromatic ring. Thus, this phenomenon is corroborated with the chemical shifts observed

for H13 and H16 in ^{1}H NMR. The ^{1}H NMR spectrum of **3** also exhibited a singlet at 2.07 ppm for the –CH_3 of free acetonitrile.

[Insert Figure 4]

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3. Conclusion

In this work, the 4-toluenesulfonyl-L-serine (**1**) ligand and two new palladium (II) mixed-ligand complexes, [Pd(4,4'-dmbipy)(tsser)] (**2**) and [Pd(5,5'-dmbipy)(tsser)].0.5CH_3CN (**3**), have been synthesized. All of these compounds were characterized by elemental analysis, IR, UV-Vis and ^{1}H NMR spectroscopy and their structures were studied by single-crystal X-ray crystallography. In the crystal structure of compound **1**, intermolecular O-H···O, N-H···O and C-H···O hydrogen bonds, in compound **2**, intermolecular O-H···O and C-H···O hydrogen bonds and in compound **3**, π-π interactions and intermolecular O-H···O, C-H···O and C-H···N hydrogen bonds are effective in the stabilization of the crystal structures and the formation of the 3D supramolecular compounds.

4. Experimental

4.1. Physical measurements and materials

All chemicals were purchased from Merck and Aldrich. Infrared spectra (4000–250 cm^{-1}) of solid samples were taken as 1% dispersion in CsI pellets using a Shimadzu-470 spectrometer. NMR was recorded on a Bruker AC-300 spectrometer for protons at 300.13 MHz in DMSO-d_6. Melting points were obtained on a Kofler Heizbank Rechart type 7841 melting point apparatus. Elemental analysis was performed using a Heraeus CHN–O Rapid analyzer. UV-Vis spectra were recorded on a Shimadzu 2100 spectrometer using a 1 cm path length cell DMSO at room temperature.

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4.2. Crystal structure determination and refinement

The X-ray diffraction measurements were made on a STOE IPDS-II diffractometer with graphite monochromated Mo-Kα radiation. For tsserH_2 (**1**), a colorless plate crystal with dimensions 0.50×0.20×0.15 mm, for [Pd(4,4'-dmbipy)(tsser)] (**2**), a yellow plate crystal with dimensions 0.12×0.08×0.08 mm and for [Pd(5,5'-dmbipy)(tsser)].0.5CH_3CN (**3**), a yellow plate crystal with dimensions 0.45×0.40×0.25 mm were mounted on glass fibers and used for data collection. Cell constants and an orientation matrix for data collection were obtained by the least-squares refinement of the diffraction data from 2952 for **1**, 4614 for **2** and 3923 for **3** unique reflections. Data were collected at 120(2) K for **1**-**3** to a maximum 2θ value of 58.30 for **1**, 58.32 for **2** and 50.00° for **3** in a series of ω scans in 1° oscillations and then integrated using the Stoe X-AREA[33] software package. The numerical absorption coefficients, μ, for Mo-Kα radiation are 0.291 mm^{-1} for **1**, 0.997 mm^{-1} for **2** and 0.952 mm^{-1} for **3**. The numerical absorption correction was applied using the X-RED[34] and X-SHAPE[35] software packages. The data were corrected for Lorentz and Polarizing effects. The structures were solved by direct methods and subsequent

differences Fourier maps and then refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters. [36] All hydrogen atoms for **1**, **2**, **3** and **4** were added at ideal positions and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}$. Atomic factors are from the International Tables for X-ray Crystallography.[37] All refinements were performed using the X-STEP32 crystallographic software package.[38]

Full crystallographic details are deposited with the Cambridge Structural Database (CCDC No 1012724 for complex **1**, 1012725 for complex **2** and 1012726 for complex **3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK.

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4.3. Synthesis of compounds

4.3.1. Synthesis of 4-toluenesulfonyl-L-serine (tsserH_2) (**1**)

4-Toluenesulfonyl-L-serine was prepared according to the procedure described previously.[18] (for synthesis details, please see Supplemental Materials)

4.3.2. Synthesis of [Pd(4,4'-dmbipy)(tsser)] (**2**)

A suspension of $PdCl_2$ (0.09 g, 0.5 mmol) in CH_3CN (50 mL) was stirred and warmed to 70 °C, to give a orange solution. Then 4,4'-dimethyl-2,2'-bipyridine (0.10 g, 0.5 mmol) in CH_3CN (10 mL) was added and the mixture stirred at 70 °C. After 10 min a mixture of 4-toluenesulfonyl-L-serine (0.13 g, 0.5 mmol) in CH_3OH (20 mL) and NaOH (2 mL, 0.50 M in water solution, 1.0 mmol) was added and the contents refluxed for 3 h. The solution was filtered

and allowed to crystallize at room temperature, whereupon yellow plate crystals were formed after one week (yield 0.21 g, 76.7%, m.p. 258 °C). IR (CsI, Cm^{-1}): 3042m, 2945m, 2922m, 1627s, 1421m, 1375s, 1265m, 1134m, 1088s, 980m, 906m, 809m, 667m, 584m, 530m, 434m, 388m, 309m, 260m. Uv-Vis. λ_{max} (DMSO, nm): 261, 304 and 314. ^{1}H NMR (DMSO-d_6, ppm): 8.85 (d, *J* = 5.7 Hz, 1H, 4,4'-dmbipy), 8.47 (s, 1H, 4,4'-dmbipy), 8.41 (s, 1H, 4,4'-dmbipy), 8.10 (d, *J* = 5.7 Hz, 1H, 4,4'-dmbipy), 7.93 (d, *J* = 7.8 Hz, 2H, ArH, tsser), 7.65-7.60 (m, 2H, 4,4'-dmbipy), 7.27 (d, *J* = 7.8 Hz, 2H, ArH, tsser), 4.89 (s, 1 H, OH, tsser), 3.83-3.76 (m,1H, CH, tsser), 3.61-3.51 (m, 2H, CH_2, tsser), 2.53 (s, 6 H, CH_3, 4,4'-dmbipy), 2.34 (s, 3 H, CH_3, tsser). Elemental analysis Calcd (%) for **2**, $C_{22}H_{23}N_3O_5PdS$: C, 48.22; H, 4.20; N, 7.67. Found: C, 47.91; H, 4.18; N, 7.63.

4.3.3. Synthesis of [Pd(5,5'-dmbipy)(tsser)].0.5CH_3CN (**3**)

The complex of **3** was prepared according to the procedure of complex **2** except using 5,5'-dimethyl-2,2'-bipyridine instead of 4,4'-dimethyl-2,2'-bipyridine in mixture of CH_3CN (60 mL) and MeOH (20 mL). Yellow plate single crystals of **3** suitable for X-ray analysis were obtained by slow evaporation of the solvent after one week (yield 0.22 g, 77.4%, m.p. 246 °C). IR (CsI, Cm^{-1}): 3051m, 2921m, 2306w, 1641s, 1514m, 1362s, 1141m, 1029s, 985m, 943m, 837m, 716m, 668m, 612m, 576m, 527m, 422m, 347m, 279m, 261m. Uv-Vis. λ_{max} (DMSO, nm): 262 and 322. ^{1}H NMR (DMSO-d_6, ppm): 8.85 (s, 1H, 5,5'-dmbipy), 8.45 (d, *J* = 8.4 Hz, 1H, 5,5'-dmbipy), 8.39 (d, *J* = 8.4 Hz, 1H, 5,5'-dmbipy), 8.16 (t, 2H, 5,5'-dmbipy), 8.04 (s, 1H, 5,5'-dmbipy), 7.92 (d, *J* = 7.5 Hz, 2H, ArH in tsser), 7.29 (d, *J* = 7.5 Hz, 2H, ArH in tsser), 4.95 (s, 1 H, OH in tsser), 3.85-3.82 (m,1H, CH in tsser), 3.63-3.56 (m, 2H, CH_2 in tsser), 2.45 (s, 3 H, CH_3 in 5,5'-

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dmbipy), 2.41 (s, 3 H, CH_3 in 5,5'-dmbipy), 2.34 (s, 3 H, CH_3 in tsser), 2.07 (s, 1.5H, CH in CH_3CN). Elemental analysis Calcd (%) for **3**, $C_{23}H_{24.5}N_{3.5}O_5PdS$: C, 48.59; H, 4.31; N, 8.62. Found: C, 48.21; H, 4.28; N, 8.55.

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Table 1 Crystallographic and structure refinement data for **1**–**3**

	1	**2**	**3**
Formula	$C_{10}H_{13}NO_5S$	$C_{22}H_{23}N_3O_5PdS$	$C_{23}H_{24.5}N_{3.5}O_5PdS$
Formula weight	259.28	547.90	568.43
Temperature /K	120(2)	120(2)	120(2)
Wavelength λ /Å	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic	Orthorhombic
Space Group	$P2_12_12_1$	$P\bar{1}$	$P2_12_12$
Crystal size /mm^3	0.11×0.10×0.09	0.12×0.08×0.08	0.45×0.40×0.25
a /Å	4.9036(10)	6.0595(12)	11.974(2)
b /Å	9.7072(19)	9.975(2)	17.892(4)
c /Å	24.168(5)	10.170(2)	10.592(2)
α /°	90	113.39(3)	90
β /°	90	101.57(3)	90
γ /°	90	96.62(3)	90
Volume / Å^3	1150.4(4)	539.6(3)	2269.2(8)
Z	4	1	2
Density (calc.) /g cm^{-1}	1.497	1.686	1.664
θ ranges for data collection	2.69-29.15	2.42-29.16	2.57-25.00
F(000)	544	278	1156
Absorption coefficient mm^{-1}	0.291	0.997	0.952
Index ranges	-5≤ h ≤ 6	-8≤ h ≤ 8	-14≤ h ≤ 12
	-11 ≤ k ≤ 13	-12 ≤ k ≤ 13	-21 ≤ k ≤ 18
	-27≤ l ≤ 33	-13≤ l ≤ 13	-12≤ l ≤ 11
Data collected	5147	5960	7014
Unique data (R_{int})	2952, 0.0364	4614, 0.0934	3923, 0.0444
Parameters, restrains	167, 0	268, 3	313, 0
Final R_1, wR_2[a] (Obs. data)	0.0398, 0.0825	0.0614, 0.1176	0.0333, 0.0838
Final R_1, wR_2[a] (All data)	0.0472, 0.0854	0.0810, 0.1360	0.0391, 0.0983
Goodness of fit on F^2 (S)	1.007	1.007	1.126
Largest diff peak and hole /e.Å^{-3}	0.369, -0.302	0.822, -0.789	0.973, -0.401

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(w(F_o^2-F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$

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Table 2 Bond distances (Å) and bond angles (°) for **1-3**

		1	
S1-N1	1.6206(18)	N1-S1-C5	109.79(10)
S1-C5	1.764(2)	C8-N1-S1	120.32(15)
O3-C9	1.204(3)	N1-C8-C9	111.49(17)
O4-C9	1.319(3)	N1-C8-C10	109.54(17)
N1-C8	1.459(3)	C9-C8-C10	109.76(17)
C8-C9	1.519(3)	O3-C9-O4	125.9(2)
C8-C10	1.529(3)	O3-C9-C8	124.4(2)
		O4-C9-C8	109.68(18)
		2	
Pd1-O3	2.007(10)	N1-Pd1-N3	99.5(5)
Pd1-N1	1.989(13)	N1-Pd1-N2	81.1(5)
Pd1-N2	2.021(14)	N3-Pd1-N2	177.3(7)
Pd1-N3	2.014(12)	C21-O3-Pd1	114.2(8)
S1-N3	1.625(13)	C20-N3-Pd1	106.6(8)
S1-C19	1.776(9)	S1-N3-Pd1	117.8(7)
O3-C21	1.268(16)	N3-S1-C19	102.7(5)
O4-C21	1.232(13)	N3-C20-C22	109.2(9)
N3-C20	1.489(16)	N3-C20-C21	109.9(9)
C20-C21	1.528(15)	O3-C21-C20	117.0(10)
O3-Pd1-N1	177.7(6)	O4-C21-O3	124.6(10)
O3-Pd1-N3	82.8(5)	N3-C20-C22	109.2(9)
O3-Pd1-N2	96.6(5)		
		3	
Pd1-O3	1.992(4)	N2-Pd1-N3	176.9(2)
Pd1-N1	2.002(4)	N1-Pd1-N3	102.39(19)
Pd1-N2	2.000(4)	N2-Pd1-N1	80.58(17)
Pd1-N3	2.020(4)	C22-O3-Pd1	115.3(3)
S1-N3	1.600(4(	C20-N3-Pd1	108.0(3)
S1-C19	1.783(6(	S1-N3-Pd1	124.6(3)
O3-C22	1.308(7(	N3-S1-C19	104.2(2)
O4-C22	1.220(7(	N3-C20-C21	107.9(4)
C20-C22	1.529(7)	N3-C20-C22	110.2(4)
N3-C20	1.483(7)	O4-C22-O3	122.3(5)
O3-Pd1-N2	94.38(18)	O3-C22-C20	115.6(4)
O3-Pd1-N1	173.87(17)	N3-C20-C21	107.9(4)
O3-Pd1-N3	82.61(17)		

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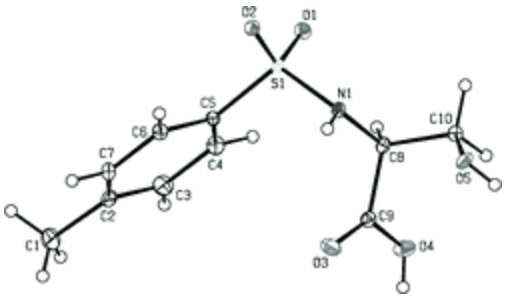

Figure 1 The labeled diagram of 4-toluenesulfonyl-L-serine (1). Thermal ellipsoids are at 50% probability level.

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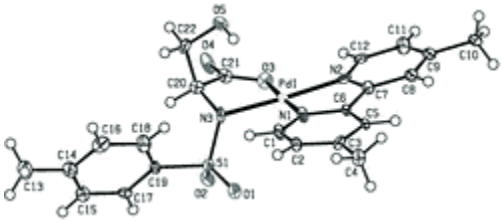

Figure 2 The labeled diagram of [Pd(4,4'-dmbipy)(tsser)] (**2**). Thermal ellipsoids are at 50% probability level.

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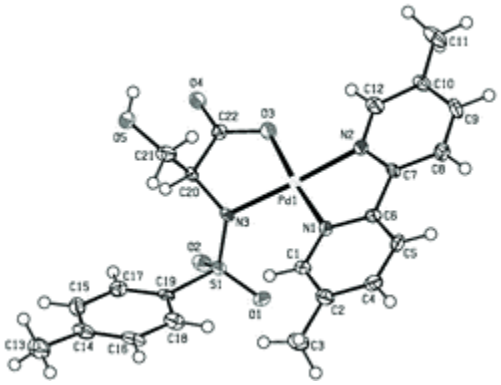

Figure 3 The labeled diagram of [Pd(5,5'-dmbipy)(tsser)] (**3**). Thermal ellipsoids are at 50% probability level.

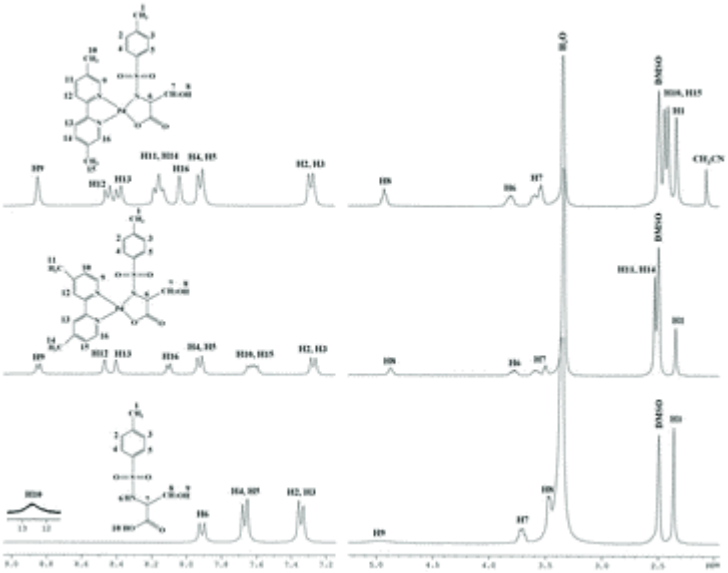

Figure 4 The ^{1}H NMR spectra of compounds **1**, **2** and **3** in DMSO-d_6.

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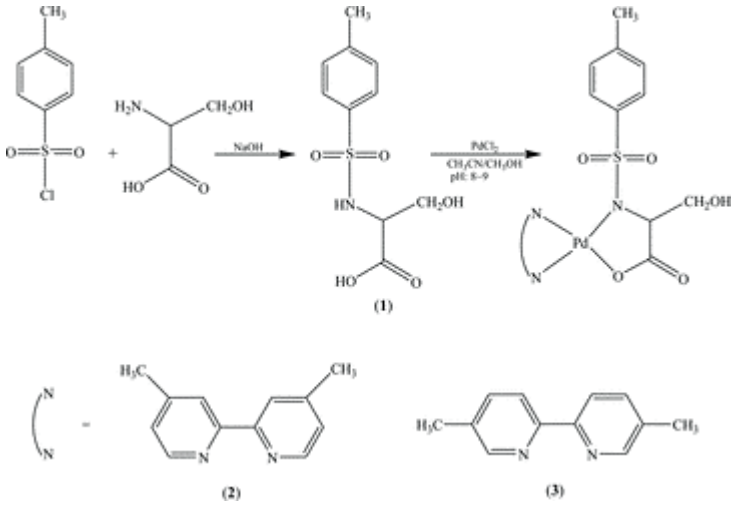

Scheme 1. The preparation method of compounds **1**-**3**.

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