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Four mono-/bi-nuclear palladium(II) complexes of triphenylphosphine and heterocyclic-N/NS ligands: Synthesis, structural characterization and luminescence properties

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ABSTRACT

The reactions of palladium(II) chloride, PPh_3 and heterocyclic-N/NS ligand in a mixture of CH_3CN (5 ml) and CH_3OH (5 ml) produced $[PdCl_2(PPh_3)(L1)]\cdot(CH_3CN)$ (**1**) (L1 = ADMT = 3-amino-5,6-dimethyl-1,2,4-triazine), $[PdCl_2(PPh_3)(L2)]$ (**2**) (L2 = 3-CNpy = 3-cyanopyridine), $[PdCl(PPh_3)(L3)]_2\cdot(CH_3CN)$ (**3**), $[PdCl(PPh_3)_2(HL3)]Cl$ (**4**) (HL3 = Hmbt = 2-mercaptobenzothiazole). The coordination geometry around the Pd atoms in these complexes is a distorted square plane. In **3**, L3 acts as a bidentate ligand, bridging two metal centers, while in **4**, HL3 appears as monodentate ligand with one nitrogen donor atom uncoordinated. Complexes **1**–**4** are characterized by IR, luminescence, NMR and single crystal X-ray diffraction analysis. All complexes exhibit luminescence in solid state at room temperature.

1. Introduction

Studies on the complexes with phosphines and heterocyclic-N/NS mixed-ligand are extensive, because of their varied structures and photophysical properties [1,2]. In this paper, our research focuses on the palladium(II) complexes of ADMT (3-amino-5,6-dimethyl-1,2,4-triazine), 3-CNPy (3-cyanopyridine) and Hmbt (2-mercaptobenzothiazole).

The heterocyclic-N ligand 3-amino-5,6-dimethyl-1,2,4-triazine is a multifunctional ligand because the triazine ring can act as nitrogen donor, and NH_2 group can act as nitrogen donor or hydrogen donor. The only reported complex containing ADMT is $[Al(CH_3)_2]_5[ADMT][Al(CH_3)_3]$, in which all the four nitrogen atoms of ADMT coordinate to aluminum atoms [3]. The palladium(II) complex of ADMT has not yet been reported.

The heterocyclic nitrogen ligand 3-cyanopyridine is widely used as a conjugated ligand in synthesizing supramolecular compounds, such as $[\{Cu(3\text{-}CNPy)_2(H_2O)\}_2\{Cu(3\text{-}CNPy)_2(H_2O)_2\}\{W(CN)_8\}_2]\cdot 6H_2O$ [4] and $Fe(3\text{-}CNPy)_2[Ag(CN)_2]_2\cdot 2/3H_2O$ [5]. $[PdCl_2(3\text{-}CNPy)_2]$ is the only reported palladium(II) complex of 3-CNpy [6].

Heterocyclic NS ligands are frequently used as bridging ligands for adjacent transition-metal sites in the design of luminescent materials, because the well match of their orbital energies can produce great delocalization of the spin electron density toward bridging atoms [7,8]. The rare earth and d^{10} metal complexes of 2-mercaptobenzothiazole, such as $Ln(mbt)_3$, $[Ag_6(mbt)_6]$ and $[Zn_4(\mu_4\text{-}O)(mbt)_6]$, exhibit intensive luminescence properties [9,10]. But the reported palladium(II) complexes of mbt $[Pd_2(mbt)_4]\cdot 1.5DMSO$ [11] and $[Pd_2(mbt)_4]\cdot CH_2Cl_2$ [12] are not luminescent.

The luminescence of palladium(II) complexes has received rare attention because the low spin d^8 palladium(II) complexes are well known quenchers [13]. Recently, we found that the heterocyclic-N ligand can enhance the luminescence of the d^{10} metal-phosphine complexes in the solid state at ambient temperature [14]. In this paper, we expanded our study to palladium(II)–PPh_3 complexes with different heterocyclic-N/NS co-ligands, and found that the coexistence of PPh_3 and heterocyclic-N/NS ligands remarkably change the luminescence property of d^8 palladium(II) complexes. Herein, four palladium(II) complexes $[PdCl_2(PPh_3)(L1)]\cdot(CH_3CN)$ (**1**), $[PdCl_2(PPh_3)(L2)]$ (**2**), $[PdCl(PPh_3)(L3)]_2\cdot(CH_3CN)$ (**3**) and $[PdCl(PPh_3)_2(HL3)]Cl$ (**4**) (L1 = ADMT; L2 = 3-CNpy; HL3 = Hmbt) are synthesized, and all the complexes exhibit luminescence in solid state at room temperature, which makes them more intriguing.

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2. Experimental

2.1. Materials and measurements

All chemical reagents are commercially available and used without furthermore treatment. FT-IR spectra (KBr pellets) were measured on a Perkin-Elmer Infrared spectrometer. C, H and N elemental analysis were carried out on a Elementar Vario MICRO CUBE (Germany) elemental analyzer.

2.2. Preparation of the complexes

2.2.1. Synthesis of [PdCl$_2$(PPh$_3$)(L1)]·(CH$_3$CN) (**1**)

Triphenlyphosphine (PPh$_3$) (0.3 mmol, 0.0788 g) and L1 (0.3 mmol, 0.0372 g) were added into the stirring solution of PdCl$_2$ (0.3 mmol, 0.0532 g) in a mixture of CH$_3$CN (5 ml) and CH$_3$OH (5 ml). Six hours later, the yellow precipitate was filtered off. Subsequent slow evaporation of the yellow filtrate resulted in the formation of yellow crystals of the title complex. *Anal.* Calc. for $C_{25}H_{26}Cl_2N_5PPd$: C, 49.7; H, 4.3; N, 11.6. Found: C, 49.6; H, 4.3; N, 11.5%. Selected IR absorptions (KBr disc, v/cm^{-1}): 3405m, 3299m, 1628s, 1534m, 1481m, 1435s, 1395m, 1714s, 1143m, 1096m, 1026w, 998w, 748m, 708m, 694s, 534s, 511m. ^{1}H NMR (DMSO, 600 MHz, ppm): 7.8–7.4 (m, 15H, phenyl-H), 3.3 (s, 2H, H$_2$O), 2.8–2.0 (m, 9H, CH$_3$CN–H, ADMT–CH$_3$–H).

2.2.2. Synthesis of [PdCl$_2$(PPh$_3$)(L2)] (**2**)

Complex **2** has been prepared following a procedure similar to that reported for **1** by adding PPh$_3$ (0.2 mmol, 0.0525 g) and L2 (0.2 mmol, 0.0208 g) into a mixture of CH$_3$CN (5 ml) and MeOH (5 ml) containing PdCl$_2$ (0.2 mmol, 0.0355 g). After slow evaporation of the yellow filtrate at ambient temperature for 1 week, a red strip shaped complex was obtained. *Anal.* Calc. for $C_{24}H_{19}Cl_2N_2PPd$: C, 53.0; H, 3.5; N, 5.2. Found: C, 53.0; H, 3.4; N, 5.0%. Selected IR absorptions (KBr disc, v/cm^{-1}): 3443m, 1632w, 1599w, 1481m, 1434s, 1191m, 1098s, 1027w, 998w, 810m, 747m, 709m, 690s, 535s, 514m, 500m. ^{1}H NMR (DMSO, 600 MHz, ppm): 8.0–7.3 (m, 19H, phenyl-H, py-H), 3.4 (s, 2H, H$_2$O), 2.6–2.5 (m, DMSO–H).

2.2.3. Synthesis of [PdCl(PPh$_3$)(L3)]$_2$·(CH$_3$CN) (**3**)

Follow the same procedure as **1**, with L1 replaced by HL3 (0.3 mmol, 0.0502 g). The crystal was obtained by slow evaporation of the red filtrate for 2 days, which was filtered off and washed with Et$_2$O to give complex **3** as a red crystal. *Anal.* Calc. for $C_{52}H_{41}Cl_2N_3P_2Pd_2S_4$: C, 52.9; H, 3.5; N, 3.6. Found: C, 52.8; H, 3.4; N, 3.5%. Selected IR absorptions (KBr disc, v/cm^{-1}): 3052w, 1571w, 1479m, 1448w, 1433s, 1383s, 1314m, 1246m, 1096s, 1028s, 1012s, 998m, 744s, 725m, 707m, 692s, 616m, 528s, 511m, 494m. ^{1}H NMR (DMSO, 600 MHz, ppm): 9.0–7.1 (m, 38H, phenyl-H), 4.4 (s, 1H, SH–H), 2.5 (m, DMSO–H), 2.08 (s, 3H, CH$_3$CN–H).

2.2.4. Synthesis of [PdCl(PPh$_3$)$_2$(HL3)]Cl (**4**)

Details of synthesis of **3** also apply to **4**, by adding PPh$_3$ (0.3 mmol, 0.0788 g) and HL3 (0.4 mmol, 0.0669 g) into a mixture of CH$_3$CN (5 ml) and MeOH (5 ml) containing PdCl$_2$ (0.3 mmol, 0.0532 g). Slow evaporation of the red filtrate for 12 days resulted in the red crystals of the title complex. *Anal.* Calc. for $C_{43}H_{35}Cl_2NP_2PdS_2$: C, 59.4; H, 4.1; N, 1.6. Found: C, 59.4; H, 4.0; N, 1.6%. Selected IR absorptions (KBr disc, v/cm^{-1}): 3437m, 1653m, 1497m, 1432s, 1386w, 1095m, 1081m, 1027s, 1012s, 749s, 692s, 526s, 511m. ^{1}H NMR (DMSO, 600 MHz, ppm): 9.1 (s, 1H, SH–H), 9.0–7.0 (m, 34H, phenyl-H), 3.3 (s, 2H, H$_2$O), 2.5 (s, DMSO–H).

2.3. Crystal structure determination and refinement

Crystals of **1**–**4** suitable for single-crystal X-ray diffraction were mounted on a Bruker Smart 1000 CCD diffractometer equipped with a graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation at 293(2) K. Semi-empirical absorption corrections were applied using SABABS program. The program SAINT [15] was used for integration of the diffraction profiles. All structures were solved by direct methods using the SHELXS program of the SHELXTL-97 package and refined with SHELXL [16]. Metal atom centers were located from the E-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinements were performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. The hydrogen atoms were generated geometrically and refined with displacement parameters riding on the concerned atoms. Crystallographic data and experimental details for structural analysis are summarized in Table 1, and selected bond lengths and angles of **1**–**4** are summarized in Table 2.

3. Results and discussion

3.1. Synthesis and characterization of complexes 1–4

Four Pd(II) complexes [PdCl$_2$(PPh$_3$)(L1)]·(CH$_3$CN) (**1**), [PdCl$_2$(PPh$_3$)(L2)] (**2**), [PdCl(PPh$_3$)(L3)]$_2$·(CH$_3$CN) (**3**) and [PdCl(PPh$_3$)$_2$(HL3)]Cl (**4**) are obtained by the one-pot reaction of the metal salts with the heterocyclic-N/NS ligand and PPh$_3$ (Scheme 1). The reaction of PdCl$_2$, PPh$_3$ with L (L = L1 or L2) in CH$_3$CN and MeOH with molar ratio 1:1:1 of Pd:P:L gave rise to complexes **1** and **2**. Interestingly, the reaction of PdCl$_2$, PPh$_3$ with HL3 in CH$_3$CN and MeOH produced the compound **3** or **4**, depending on the molar ratio of Pd:P:HL3 we choose (the ratio is 1:1:1 for **3** and 3:3:4 for **4**). The molar ratio of Pd:P:L in complexes **1**–**3**, agrees with that in the starting materials, while the molar ratio of Pd:P:L of complex **4** is not as expected.

All the four complexes are air-stable. They are insoluble in diethyl ether but soluble in the common polar solvents such as methanol, ethanol, dichloromethane, acetonitrile, dimethylsulfoxide and dimethylformamide.

The complexes have been characterized by the elemental analyses, together with IR, NMR and the single crystal X-ray diffraction. In the four IR spectra, the following absorptions can be assigned to C=N ring stretching vibrations: the absorptions at 1481 and 1435 cm^{-1} (for **1**), 1481 and 1434 cm^{-1} (for **2**), 1479 and 1433 cm^{-1} (for **3**) and 1478 and 1434 cm^{-1} (for **4**). The absorptions of the range 3211–3405 in the spectrum of **1** can be assigned to NH$_2$ stretching vibrations. The absorption at 2237 cm^{-1} in the spectrum of **2** can be assigned to conjugated C≡N stretching vibration. The P–C vibrations of the PPh$_3$ moiety are found around 690 cm^{-1}.

3.2. Single crystal X-ray studies

3.2.1. Crystal structure of complexes 1 and 2

The asymmetric unit of each crystal structure comprises [PdCl$_2$(PPh$_3$)(L)] (L = L1 for **1** and L = L2 for **2**) molecule. The palladium(II) atom in each unit is bonded to one nitrogen of L1 or L2, one phosphorous of PPh$_3$ and two chloride atoms in a slightly distorted square-planar coordination (Figs. 1 and 2). In complex **1**, L1 acts as a monodentate ligand, while in [Al(CH$_3$)$_2$]$_5$[ADMT][Al(CH$_3$)$_3$], L1 (L1 = ADMT) adopts tetradentate coordination fashion [3]. In complex **2**, L2 is a monodentate ligand, just like in other reported similar complexes [4,5].

Table 1
Crystal data for complex **1**–**4**.

Compound	1	2	3	4
Formula	$C_{25}H_{26}Cl_{2}N_{5}PPd$	$C_{24}H_{19}Cl_{2}N_{2}PPd$	$C_{52}H_{41}Cl_{2}N_{3}P_{2}Pd_{2}S_{4}$	$C_{43}H_{35}Cl_{2}NP_{2}PdS_{2}$
Formula weight	603.78	543.68	1181.76	869.08
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*P*2(1)/*c*	*P*2(1)/*n*	*P*2(1)/*n*	*P*2(1)/*c*
a (Å)	16.2949(15)	9.6810(16)	16.1700(17)	13.9240(13)
b (Å)	10.6440(10)	13.5181(16)	13.2351(11)	15.0671(16)
c (Å)	17.0161(16)	12.2169(13)	24.7630(20)	21.9602(20)
β (°)	117.135(2)	13.6608(15)	108.459(1)	120.460(2)
V (Å^3)	2626.5(4)	2250.9(4)	5026.8(8)	3971.3(4)
Z	4	4	4	4
D_{calc} (g/cm^3)	1.529	1.604	1.562	1.454
μ (mm^{-1})	0.994	1.147	1.091	0.819
R_1 and wR_2	0.0386/0.1031	0.0317/0.0989	0.0597/0.2612	0.0501/0.1027
T (K)	298(2)	298(2)	298(2)	298(2)

Table 2
Selected bond lengths (Å) and angles (°) for complex **1**–**4**.

Complex ***1***			
Pd(1)–N(1)	2.023(3)	P(1)–Pd(1)–Cl(2)	179.1(4)
Pd(1)–P(1)	2.374(7)	Cl(1)–Pd(1)–Cl(2)	92.1(4)
Pd(1)–Cl(1)	2.305(1)	C(12)–P(1)–Pd(1)	107.2(1)
Pd(1)–Cl(2)	2.368(1)	C(6)–P(1)–Pd(1)	115.5(1)
N(1)–Pd(1)–P(1)	91.6(9)	C(18)–P(1)–Pd(1)	114.9(1)
N(1)–Pd(1)–Cl(1)	178.2(9)	C(3)–N(1)–Pd(1)	123.7(3)
P(1)–Pd(1)–Cl(1)	87.1(4)	N (2)–N(1)–Pd(1)	116.2(2)
N(1)–Pd(1)–Cl(2)	89.1(9)		
Complex ***2***			
Pd(1)–N(1)	2.141(3)	P(1)–Pd(1)–Cl(2)	89.2(4)
Pd(1)–P(1)	2.253(1)	Cl(1)–Pd(1)–Cl(2)	178.3(5)
Pd(1)–Cl(1)	2.287(1)	C(12)–P(1)–Pd(1)	106.2(1)
Pd(1)–Cl(2)	2.308(1)	C(7)–P(1)–Pd(1)	117.2(1)
N(1)–Pd(1)–P(1)	179.3(1)	C(19)–P(1)–Pd(1)	113.4(1)
N(1)–Pd(1)–Cl(1)	88.4(1)	C(5)–N(1)–Pd(1)	123.9(3)
P(1)–Pd(1)–Cl(1)	91.6(4)	C(1)–N(1)–Pd(1)	119.1(3)
N(1)–Pd(1)–Cl(2)	90.8(1)		
Complex ***3***			
Pd(1)–N(1)	2.049(7)	Cl(2)–Pd(2)–P(2)	92.3(1)
Pd(1)–P(1)	2.278(2)	N(2)–Pd(2)–S(2)	89.0(2)
Pd(1)–Cl(1)	2.291(2)	Cl(2)–Pd(2)–S(2)	86.3(1)
Pd(1)–S(4)	2.371(2)	P(2)–Pd(2)–S(2)	176.8(9)
Pd(2)–N(2)	2.018(7)	C(1)–N(1)–Pd(1)	123.3(6)
Pd(2)–Cl(2)	2.296(3)	C(2)–N(1)–Pd(1)	124.6(6)
Pd(2)–P(2)	2.298(3)	C(8)–N(2)–Pd(2)	122.9(6)
Pd(2)–S(2)	2.365(3)	C(9)–N(2)–Pd(2)	124.1(6)
N(1)–Pd(1)–P(1)	94.2(2)	C(21)–P(1)–Pd(1)	112.8(3)
N(1)–Pd(1)–Cl(1)	176.1(2)	C(27)–P(1)–Pd(1)	115.7(3)
P(1)–Pd(1)–Cl(1)	87.5(9)	C(15)–P(1)–Pd(1)	109.6(3)
N(1)–Pd(1)–S(4)	92.3(2)	C(39)–P(2)–Pd(2)	112.7(4)
P(1)–Pd(1)–S(4)	173.3(9)	C(45)–P(2)–Pd(2)	112.4(3)
Cl(1)–Pd(1)–S(4)	85.9(9)	C(33)–P(2)–Pd(2)	116.4(3)
N(2)–Pd(2)–Cl(2)	175.2(2)	C(1)–S(2)–Pd(2)	106.4(3)
N(2)–Pd(2)–P(2)	92.4(2)	C(8)–S(4)–Pd(1)	105.7(3)
Complex ***4***			
Pd(1)–S(2)	2.319(1)	P(1)–Pd(1)–P(2)	174.5(5)
Pd(1)–P(1)	2.361(1)	C(1)–S(2)–Pd(1)	103.8(2)
Pd(1)–Cl(1)	2.341(1)	C(8)–P(1)–Pd(1)	118.3(2)
Pd(1)–P(2)	2.374(1)	C(14)–P(1)–Pd(1)	114.3(2)
S(1)–Pd(1)–Cl(1)	177.9(5)	C(20)–P(1)–Pd(1)	108.6(2)
S(2)–Pd(1)–P(1)	92.3(5)	C(38)–P(2)–Pd(1)	106.6(2)
Cl(1)–Pd(1)–P(1)	88.4(5)	C(26)–P(2)–Pd(1)	114.2(2)
S(2)–Pd(1)–P(2)	91.4(5)	C(32)–N(1)–Pd(1)	118.8(2)
Cl(1)–Pd(1)–P(2)	87.8(5)		

The angles around Pd(II) atoms in the coordination sphere, which are in the range 87.1(4)–92.1(4)° for **1** and in the range 88.4(1)–91.6(4)° for **2**, are close to the expected value 90° and similar to the corresponding angles in compounds $[(PPh_3)Pd(HL)Cl]Cl\cdot2CH_3CN$, $[(PPh_3)Pd(HL)I]Cl\cdot1/2H_2O$ (HL = 4-amino-5-methyl-2*H*-1,2,4-triazole-3(4*H*)-thione) [17].

All bond distances are within the expected values. The Pd–N bonds (2.023(3) Å for **1**, 2.141(3) Å for **2**) agree with the corresponding distances in compounds $[Pd(py)_4]Cl_2\cdot1/2H_2O$ [21] and [Pd(dmba)(N10-9AA)(PPh_3)] [18]. In complex **1**, the hydrogen bond N4H4B…Cl1 helps to stabilize the structure. Here the distance N4…Cl1 is 3.287 Å and the angle N4–H4B–Cl1 is 160.9°.

3.2.2. Crystal structure of complexes 3 and 4

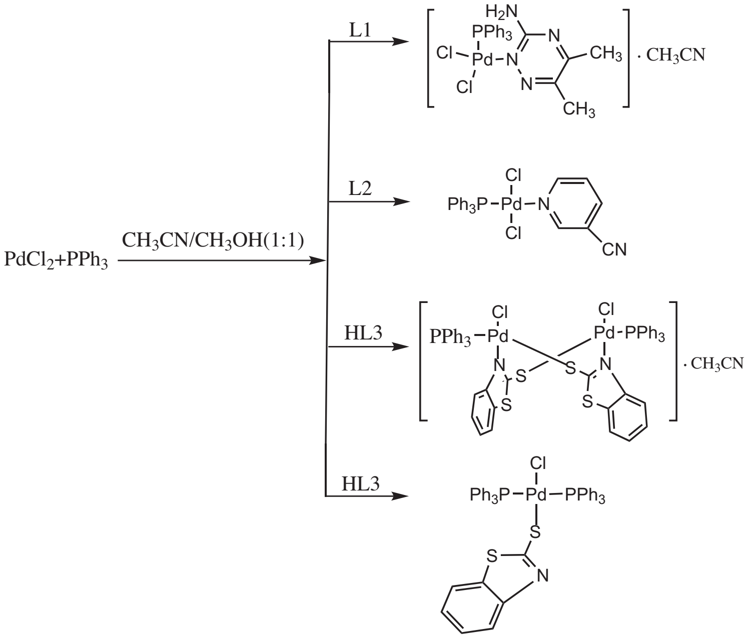
The structure of $[PdCl(PPh_3)(L3)]_2\cdot(CH_3CN)$ (**3**) consists of one dimeric unit and one CH_3CN solvent molecule (Fig. 3). Each palladium atom is bonded to one thiolate bridging sulfur, one bridging nitrogen, one phosphorus of triphenylphosphine and one chloride in a distorted square-planar geometry. The two planar units (Pd1–N1–P1–Cl1–S4 and Pd2–N2–P2–Cl2–S2) are joined via two bridging mbt ligands to form an eight-membered ring. The Pd…Pd distance 3.6728(1) Å, which is much longer than the corresponding distance in other Pd–L3 complexes, such as complex $[Pd_2(mbt)_4]\cdot1.5DMSO$ (Pd…Pd distance 2.747(2) Å) [11] and $[Pd_2(mbt)_4]\cdot CH_2Cl_2$ (Pd…Pd distance 2.756(5) Å) [12], shows that there exists no Pd–Pd bond in the complex.

The angles (85.9(9)–94.2(2)°) in the coordination sphere of the metal atom show deviation from the ideal 90°, which is similar to the compounds **3d**, **5a**, **5c**, **6a**, 6b and **7a** in [19]. Due to the steric stress between two L3 ligands located on the same side of the Pd…Pd axis, the square-planar structure in **3** is much more distorted than the corresponding structure in complexes **1** and **2**.

The values of the bite angles N–Pd–S are 92.3(2)° (N1–Pd1–S4) and 89.0(2) (N2–Pd2–S2), which are similar to those found for other dinuclear complexes such as $[Pd(SCN)(\mu\text{-med})]_2\cdot0.5CH_3CN$ (87.9(2)° and 90.2(1)°, $[Pd(N_3)(\mu\text{-med})]_2$ (92.4(1)° and 93.5(1)°), $[PdCl(\mu\text{-med})]_2$ (91.5(1)° and 92.1(9)°) [20] and $[Pd(\mu\text{-med})(PPh_3)]_2$ (84.1(9)°) [18]. [Hmed = N-2-mercaptoethyl)-3,5-dimethylpyrazole].

In the crystal structure of complex **4**, the unit cell consists of one $[PdCl(PPh_3)_2(HL3)]^+$ cation and one chloride anion. The metal center allows the formation of a distorted planar square with four vertex occupied by two phosphorus atoms of two PPh_3, one thiolate-sulfur atom of mbt and one chloride. The perspective view of **4** is shown in Fig. 4.

In complex **4**, the bridging coordination of HL3 is broken, leaving the thiazole-nitrogen uncoordinated. The Pd–S bond distance (Pd1–S2 = 2.319(1) Å) is shorter than those in complex **3** (Pd1–S4 = 2.371(2), Pd2–S2 = 2.365(3) Å), but both the Pd–P distances (Pd1–P1 = 2.361(1), Pd1–P2 = 2.374(1) Å) and the Pd–Cl distance (Pd1–Cl1 = 2.341(1) Å) are much longer than the corresponding distances in complex **3** (Pd1–P1 = 2.278(2), Pd2–P2 = 2.298(3), Pd1–Cl1 = 2.291(2), Pd2–Cl2 = 2.296(3) Å). This can be attributed



(L1= 3-Amino-5,6-dimethyl-1,2,4-triazine, L2=3-cyanopyridine), HL3=2-Mercaptobenzothiazole

Scheme 1. The routine of synthesis for complexes **1**–**4**.

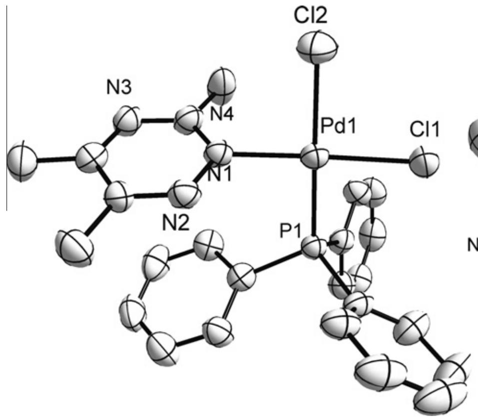


Fig. 1. Perspective view of complex **1**. All the hydrogen atoms are omitted for clarity.

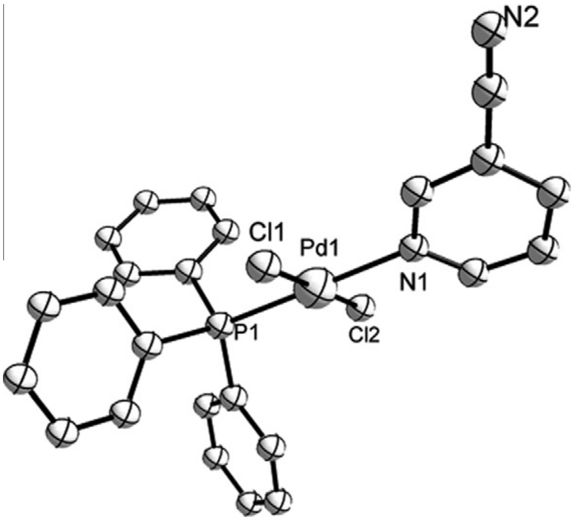


Fig. 2. Perspective view of complex **2**. All the hydrogen atoms are omitted for clarity.

to the need to accommodate the bulky triphenylphosphine groups. The Pd–P distances are similar to those observed in complex $Pd(CO_2CH_3)(ONO_2)(PPh_3)_2$ (Pd–P1 = 2.349(3), Pd–P2 = 2.364(3) Å) [21].

3.3. Emission spectra of complexes

In this work, photoluminescence spectra in the solid state at room temperature of complexes **1**–**4** and free ligands L1, L2 and HL3 have been measured (Figs. S1–S7). Free ligands PPh_3, L1, L2 and HL3 display emission with maxima at 447 nm [22], 400 nm (λ_{ex} = 329 nm for L1), 405 nm (λ_{ex} = 333 nm for L2) and 402 nm (λ_{ex} = 337 nm for HL3), respectively. All the compounds **1**–**4** possess fluorescence properties. Compounds **1** and **2** show emission with maxima at 439 nm and 437 nm, respectively. The resemblance of the emission spectrum of the compound **1** or **2** with that of the free ligand PPh_3 indicates that the luminescence of the compound **1** or **2** is PPh_3-based emission. Each of compounds **3** and **4** shows two emission peaks (416 and 438 nm for **3**, 419 and 438 nm for **4**). The emission peaks of compounds **3** and **4** are blue-shifted with respect to the free ligand PPh_3 and are red-shifted with respect to the free ligand HL_3. So it is easy to conclude that the emission spectra of compounds **3** and **4** can be assigned to ILCT (intra-ligand charge transfer) based on both HL3 and PPh_3 ligands. The shifts of the emission bands of compounds **1**–**4** can be attributed to the coordination action of L1, L2, HL3 and PPh_3 on palladium(II) atoms. For all the four palladium complexes, the absence of the low-energy emission is likely due to a higher energy difference between the metal and ligand orbitals. Though it seems that the emission spectra of **1** and **2** are not related to the heterocyclic N ligand (L1 or L2), the presence of L1 (or L2) is very

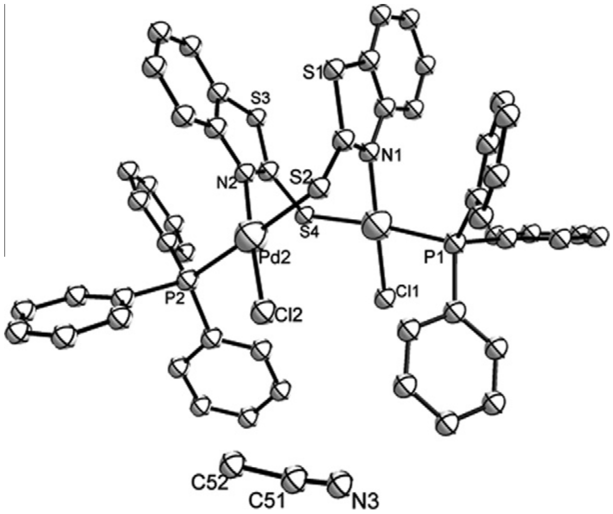


Fig. 3. Perspective view of complex **3**. All the hydrogen atoms are omitted for clarity.

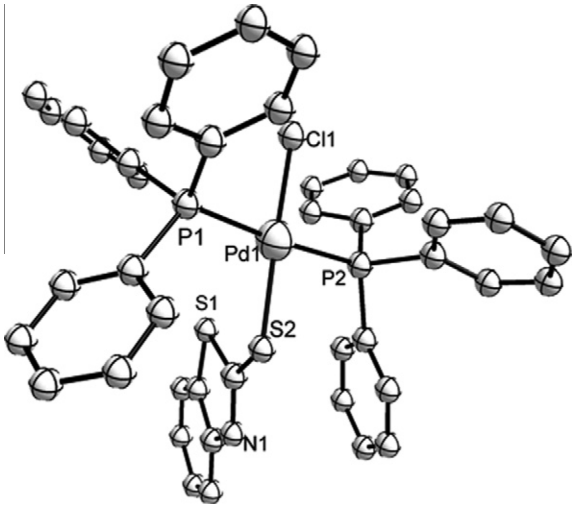


Fig. 4. Perspective view of complex **4**. All the hydrogen atoms are omitted for clarity.

important for the products to have luminescence. From the luminescence of complexes **1**–**4** and similar compounds [23], we can know that the coexistence of PPh_3 and heterocyclic-N/NS ligands brings remarkable change in luminescence property of d^8 palladium(II) complexes.

3.4. NMR spectra of complexes

The ^1H NMR and ^{31}P NMR spectra of complexes **1**–**4** were measured at room temperature in DMSO solution. In the ^1H NMR spectra of complexes **1**–**4**, the broad multiplet assigned to signals of aromatic protons are in the range 7.4–7.8 ppm, 7.3–8.0 ppm, 7.1–9.0 ppm, and 7.0–9.0 ppm, respectively. In ^1H NMR spectra of complex **1**, there is another broad multiplet in the range 2.0–2.8 ppm, which is assigned to triazine–methyl protons and acetonitrile protons. There is a singlet at 2.1 ppm in complex **3**, which is attributed to acetonitrile protons. The ^1H NMR spectrum of complex **4** shows the singlet at 9.1 ppm, which is attributed to the signal of mercapto-proton.

From the ^{31}P NMR spectra we can see that **1**, **2** and **4** phosphorous signal splittings are 24.7 and 25.0 ppm for **1**, 26.9 and 27.1 ppm for **2** and 24.5, 26.2 and 27.2 ppm for **4**. In the ^{31}P NMR spectrum of **3**, only one single resonance signal is found (26.1 ppm). The ^{31}P spectra reveal that the structures of complexes **1**, **2**, **4** in solvent DMSO-d^6 are not consistent with observed solid state structures. Binuclear Pd(II) complex **3** is stable in DMSO-d^6 solution, while mononuclear Pd(II) complexes **1**, **2** and **4** are unstable. The instability of compounds **1**, **2**, **4** in DMSO-d^6 is probably the result of substitution of N/NS ligands or chlorine atoms by the molecules of the solvent DMSO [24]. This hypothesis is consistent with the fact that the strong coordination ability of DMSO-d^6 with metal Pd(II) atom cleaves the metal-nitrogen (sulfur or chloride) bond leaving free ligand molecules [25]. Magnetic resonance investigation of complexes containing PPh_3 and N/NS ligands provides some important information about the structure and stability of these compounds. But the unknown dissociated byproducts bring about complicated NMR spectral patterns [26].

4. Conclusion

In conclusion, we have synthesized and characterized three mononuclear and one binuclear Pd(II)–PPh_3 complexes containing different heterocyclic N/NS ligands, including 3-amino-5,6-dimethyl-1,2,4-triazine (ADMT), 3-cyanopyridine (3-CNpy) and 2-mercaptobenzothiazole (Hmbt). Complex **1** is the first Pd(II) complex of ADMT. We found that ADMT and 3-CNpy act as monodentate ligands. Hmbt acts as a bidentate NS-bridging ligand through its thiolate-sulfur and thiazole-nitrogen atoms, while its deprotonated species mbt acts as a monodentate ligand. Complexes **3** and **4** are obtained from the same starting materials with different molar ratio of Pd:Hmbt. All the four Pd(II) complexes exhibit luminescence properties. The coexistence of PPh_3 and heterocyclic-N/NS ligands remarkably enhances the luminescence property of d^8 palladium(II) complexes. In solution, mononuclear complexes (**1**, **2** and **4**) show complicated ^{31}P NMR spectra, which are attributed to the reaction of DMSO solvent toward Pd(II) atoms.

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Appendix A. Supplementary data

CCDC 807177, 807180, 807178 and 807179 contain the supplementary crystallographic data for the compounds **1**–**4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2011.10.001.

References

[1] R. Starosta, M. Puchalska, J. Cybínska, M. Barys, A.V. Mudring, Dalton Trans. 40 (2011) 2459.
[2] S.H. Fan, A.G. Zhang, C.C. Ju, L.H. Gao, K.Z. Wang, Inorg. Chem. 49 (2010) 3752.

[3] M.F. Self, P.T. William, R.H. Gregory, J. Coord. Chem. 24 (1991) 69.

[4] S. Ohkoshi, Y. Arimoto, T. Hozumi, H. Seino, Y. Mizobe, K. Hashimoto, Chem. Commun. (2003) 2772.

[5] A. Galet, V. Niel, M.M.C. Munñoz, J.A. Real, J. Am. Chem. Soc. 125 (2003) 14224.

[6] M.N. Kopylovich, J. Lasri, M.F.C.G. Silva, A.J.L. Pombeiro, Dalton Trans. (2009) 3074.

[7] Q.H. Jin, J.J. Sun, J.Q. Wu, Y.C. Dai, C. Li, X.M. Lu, J. Chem. Cryst. 40 (2010) 310.

[8] (a) J.K. Cheng, Y.G. Yao, J. Zhang, Z.J. Li, Z.W. Cai, X.Y. Zhang, Z.N. Chen, Y.B. Chen, Y. Kang, Y.Y. Qin, Y.H. Wen, J. Am. Chem. Soc. 126 (2004) 7796;
(b) C. Kimblin, B.M. Bridgewater, D.G. Churchill, T. Hascall, G. Parkin, Inorg. Chem. 39 (2000) 4240;
(c) S. Perruchas, K. Boubekeu, Dalton Trans. (2004) 2394;
(d) X.H. Bu, W.F. Hou, M. Du, W. Chen, R.H. Zhang, Cryst. Growth Des. 2 (2002) 303;
(e) N.R. Brooks, A.J. Blake, N.R. Champness, J.W. Cunningham, P. Hubberstey, M. Schroder, Cryst. Growth Des. 1 (2001) 395.

[9] M.A. Katkova, A.V. Borisov, G.K. Fukin, E.V. Baranov, A.S. Averyushkin, M.N. Bochkarev, Inorg. Chim. Acta 359 (2006) 4289.

[10] S.C. Chen, R.M. Yu, Z.G. Zhao, S.M. Chen, Q.S. Zhang, X.Y. Wu, F. Wang, C.Z. Lu, Cryst. Des. Growth. 10 (2010) 1155.

[11] E.J. Gao, K.H. Wang, X.F. Gu, Y. Yu, Y.G. Sun, W.Z. Zhang, H.X. Yin, Q. Wu, M.C. Zhu, X.M. Yan, J. Inorg. Biochem. 101 (2007) 1404.

[12] S. Vuoti, M. Haukka, J. Pursiainen, Acta Crystallogr., Sect. C63 (2007) m601.

[13] J.S. Yang, S.Y. Chiou, K.L. Liau, J. Am. Chem. Soc. 124 (2002) 2518.

[14] Q.H. Jin, L.L. Song, K.Y. Hu, L.L. Zhou, Y.Y. Zhang, R. Wang, Inorg. Chem. Commun. 13 (2010) 62.

[15] G.M. Sheldrick, SHELXS-97 and SHELXL-97, Software for Crystal Structure Analysis, Siemens Analytical X-ray Instruments Inc., Wisconsin, Madison, USA, 1997.

[16] G.M. Sheldrick, SHELXTL NT Version 5.1, Program for Solution and Refinement of Crystal Structures, University of Göttingen, Germany, 1997.

[17] G. Mitra, B. Samira, M. Masoomeh, R. Babak, H.M. Hassan, M. Effat, N. Bernhard, Polyhedron 29 (2010) 3036.

[18] J. García-Antón, J. Pons, X. Solans, M. Font-Bardía, J. Ros, Inorg. Chim. Acta 357 (2004) 571.

[19] J. Martınez, L.A. Adrio, J.M. Antelo, J.M. Ortigueira, M.T. Pereira, J.J. Fernandez, A. Fernandez, J.M. Vila, J. Organomet. Chem. 691 (2006) 2721.

[20] J. García-Antón, J. Pons, X. Solans, M. Font-Bardía, J. Ros, Inorg. Chim. Acta 355 (2003) 87.

[21] E. Amadio, G. Cavinato, A. Dolmella, L. Toniolo, Inorg. Chem. 49 (2010) 3721.

[22] F.F. Li, J.F. Ma, J. Yang, H.Q. Jia, N.H. Hu, J. Mol. Struct. 787 (2006) 106.

[23] J. Ruiz, J. Lorenzo, C. Vicente, G. Lopez, J.M. Lopez-de-Luzuriaga, M. Monge, F.X. Aviles, D. Bautista, V. Moreno, A. Laguna, Inorg. Chem. 47 (2008) 6990.

[24] E. Bednarek, J. Sitkowski, R. Kawęcki, L. Kozerski, W. Bocian, L. Pazderskic, W. Priebed, Dalton Trans. (2008) 4129.

[25] (a) S.F. Liu, R. Peloso, P. Braunstein, Dalton Trans. 39 (2010) 2563;
(b) M. Juribašić, M. Cúrić, K. Molčanov, D. Matković-Čalogović, D. Babić, Dalton Trans. 39 (2010) 8769;
(c) M. Pourshahbaz, M. Irandoust, E. Rafiee, M. Joshaghani, Polyhedron 28 (2009) 609.

[26] L. Tušek-Božić, A. Lyčka, Magn. Reson. Chem. 40 (2002) 175.