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Synthesis, structures and spectroscopic properties of platinum complexes containing orthometalated 2-phenylpyridine

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ABSTRACT

The synthesis, structure and spectroscopy of a series of luminescent orthometalated square planar platinum(II) complexes are reported. Reaction of K_2PtCl_4 with one mole equivalent of 2-phenylpyridine (ppyH) in 2-ethoxyethanol and water (1:1 ratio) resulted in the formation of chloro-bridged dimeric precursor $[Pt_2(\mu\text{-Cl})_2(ppy)_2]$, which on further reactions with various anionic one-, two- and three-atom ancillary ligands, having O/N/S donors, yielded mono- and bi-nuclear platinum(II) complexes. Platinum(III) complexes of composition $[Pt_2Cl_2(\mu\text{-Epy})_2(ppy)_2]$ have been isolated with pyE^- (E = O or S) ligands. These complexes have been characterized by elemental analysis, NMR (^1H, ^{31}P, ^{195}Pt) and absorption spectroscopy. The complexes $[Pt_2(\mu\text{-N}^\frown N)_2(ppy)_2]$ ($N^\frown N$ = pyrazole and 3,5-dimethylpyrazole); $[Pt(S^\frown S)(ppy)]$ ($S^\frown S$ = ethylxanthate and diisopropyldithiophosphate); $[Pt_2Cl_2(\mu\text{-Epy})_2(ppy)_2]$ (Epy = 2-pyridinol {Opy} and 2-mercaptopyridine {Spy}) and [PtCl(ppy)(PhNC(Me)NHPh)] have been structurally characterized by X-ray crystallography.

1. Introduction

Orthometalated platinum group metal complexes have been extensively investigated [1,2] and have been used widely in many fields, such as organic synthesis [3,4], metallomesogens [5–7], photo-catalysts [8], opto-electronic devices [9–11] and building blocks for self-assembled molecules [12]. Orthometalated platinum complexes in particular have attracted much attention recently due to their interesting photophysical properties [13] which can be exploited for chemosensors, light emitting diodes, etc. applications. Although a number of platinum complexes are luminescent [13–16], orthometalated complexes based on 2-arylpyridines exhibit promising photophysical properties as many of them are emissive in solution under ambient conditions [13].

Emission from metalated 2-arylpyridine platinum complexes in solution has been assigned to ligand centered (LC) and/or metal-to-ligand charge transfer (MLCT) states. Orthometalated ligands help in raising the energy gap (ΔE) between lowest lying excited state [LC (π–π^*) and/ or MLCT (d–π^*)] and high energy antibonding $d_{x^2-y^2}$ orbital to an extent that they are not thermally accessible (ΔE > kT). Thus the emission colors (i.e. ΔE) in orthometalated 2-phenylpyridine complexes of platinum(II) can be tuned from blue-green to orange-red by appropriately substituting either the phenyl [17] and/or pyridyl [17,18] rings of 2-phenylpyridine. Substitution by an electron-withdrawing and -donating group in the phenyl ring leads to blue and red shifts, respectively in the emission spectra [17]. Substitution of electron donating groups (Me or Me_2N) at 4-position of the pyridyl ring results in to hypsochromic shift in the emission spectra [17]. Ancillary ligands in orthometalated 2-arylpyridine complexes of platinum(II) also play a crucial role on photophysical properties. For instance, $[Pt(ppy)Cl_2]^-$ (Hppy = 2-phenylpyridine) is not luminescent in solution at room temperature whereas [Pt(ppy)(Hppy)Cl] is luminescent under similar conditions [19]. Much of the studies on role of photophysical properties of orthometalated 2-arylpyridine type ligand complexes of platinum(II) are concerned with β-diketonate derivatives [17,18,20,21].

In the above perspective the present investigation was undertaken to synthesize orthometalated 2-phenylpyridine platinum(II) complexes with a variety of ancillary ligands (anionic one-, two- and three-atom ligands having O/N/S donors) and identify the nature of resulting complexes. The results of this investigation are reported herein.

2. Experimental

2.1. General procedures and instrumentation

Solvents were dried by standard methods with subsequent distillation under nitrogen. All reactions were carried out in Schlenk flasks under a nitrogen atmosphere. Melting points were determined in capillary tubes and are uncorrected. IR spectra were recorded as Nujol mulls between CsI plates on a Bomem MB-102

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FT-IR spectrometer. Elemental analyses were carried out on a Carlo-Erba EA-1110 CHN-O instrument. ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ and $^{195}Pt\{^{1}H\}$ NMR spectra were recorded on a Bruker DPX-300 and Avance II-300 NMR spectrometers operating at 300, 75.47, 121.5 and 64.29 MHz, respectively. Chemical shifts are relative to internal chloroform peak (δ 7.26 ^{1}H and 77.0 for ^{13}C), external 85% H_3PO_4 for $^{31}P\{^{1}H\}$ and Na_2PtCl_6 for $^{195}Pt\{^{1}H\}$. Absorption spectra were recorded on a Chemito Spectrascan UV 2600 spectrophotometer. Emission spectra were recorded in dichloromethane on an Edinburgh Instruments' FLSP 920 system attached with 450 W Xe lamp as excitation source and red sensitive PMT as detector.

2.2. Synthesis of complexes

2.2.1. Synthesis of [$Pt_2(\mu$-$Cl)_2(ppy)_2$] (1)

To an aqueous solution (20 mL) of K_2PtCl_4 (996 mg, 2.40 mmol) was added 2-phenylpyridine (372 mg, 2.41 mmol) in 20 mL 2-ethoxyethanol. A clear red solution was obtained, which was heated at 70 °C for 8 h whereupon a greenish solid separated out. The solid was filtered through a G-3 assembly, washed with distilled water (2 × 10 mL), acetone (2 × 5 mL) followed by dichloromethane (2 mL) (608 mg, 66%). The acetone-dichloromethane washings on drying gave greenish yellow complex, [Pt(ppy)(Hppy)Cl] (**2**), (115 mg, 9%) as identified by ^{195}Pt NMR. mp: >280 °C. Anal. Calc. for $C_{22}H_{16}Cl_2N_2Pt_2$: C, 34.3; H, 2.0; N, 3.6. Found: C, 34.2; H, 1.9; N, 3.6%.

2.2.2. Synthesis of [$Pt_2(\mu$-$SEt)_2(ppy)_2$] (4)

To a dichloromethane (4 mL) suspension of **1** (103 mg, 0.13 mmol) was added 3 drops of pyridine to get a clear yellow solution. To this an excess of ethylmercaptan (3 drops) was added and stirred for 4 h. The solvent was evaporated under vacuum and the residue was washed with methanol (3 × 3 mL) and dried in vacuo. The residue was dissolved in dichloromethane and passed through a short Florisil column. Slow evaporation of the solvent afforded yellow crystals (83 mg, 76%), mp: 233 °C. Anal. Calc. for $C_{26}H_{26}N_2Pt_2S_2$: C, 38.0; H, 3.2; N, 3.4; S, 7.8. Found: C, 37.9; H, 3.2; N, 3.3; S, 7.4%. UV–Vis (CH_2Cl_2) λ_{max} in nm: 256 (49 800); 317 (8500); 328 (8800); 367 (8500). ^{1}H NMR ($CDCl_3$): δ = 1.36, 1.65 (each t, 7.2 Hz, SCH_2*Me*, *cis* isomer); 1.58 (t, 7.2 Hz, SCH_2*Me*, *trans* isomer); 2.93–3.11 (m, SCH_2-, *cis* and *trans* isomers); 7.21–7.89 (m, C_6H_4, CH-3,4,5 (py); *cis* and *trans* isomers); 8.90, 9.11(each d, 5 Hz, H-6 py, *cis* isomer); 9.05 (d, 5 Hz, H-6 py, *trans* isomer).

2.2.3. Synthesis of [$Pt_2(\mu$-$pz)_2(ppy)_2$] (5)

To a dichloromethane suspension of [$Pt_2(\mu$-$Cl)_2(ppy)_2$] (396 mg, 0.51 mmol) was added NaOMe (2.16 mL (0.46 N), 55 mg, 1.0 mmol) and stirred for 15 min. Subsequently a methanolic solution of pyrazole (73 mg, 1.0 mmol) was added and the whole reaction mixture was stirred for additional 3 h. The solvents were evaporated under vacuum and the residue was extracted with dichloromethane. The extract was concentrated and hexane (2 mL) was added and on cooling ~5 °C gave yellow crystals which were decanted and washed with dichloromethane (217 mg, 51%). mp: 247 °C (dec., darkens above 240 °C). Anal. Calc. for $C_{28}H_{22}N_6Pt_2$: C, 40.4; H, 2.6; N, 10.1. Found: C, 40.7; H, 2.2; N, 9.8%. UV–Vis (CH_2Cl_2) λ_{max} in nm: 256 (43 500); 284 (25 100); 328 (12 300); 356 (9900); 406 (2900). ^{1}H NMR ($CDCl_3$): δ = 6.42 (t, 2 Hz, H-4 (pz)); 6.48 (m); 6.70–6.85 (m); 7.09 (d, 7 Hz); 7.45–7.50 (m); 7.62 (br); 7.98–8.15 (m).

2.2.4. Synthesis of [$Pt_2(\mu$-$dmpz)_2(ppy)_2$] (6)

To a THF solution of dmpzH (26 mg, 0.26 mmol) excess of NaH was added and stirred for 1 h. To this reaction mixture [$Pt_2(\mu$-$Cl)_2(ppy)_2$] (103 mg, 0.13 mmol) was added and was further stirred for 1 h. The solvent was evaporated to obtain yellow-orange solid. The product was extracted with THF by passing through a Florisil column. The filtrate was concentrated and acetone (1 mL) was added which on cooling ~5 °C yielded yellow crystals (75 mg, 63%). mp: above 290 °C. Anal. Calc. for $C_{32}H_{30}N_6Pt_2$: C, 43.2; H, 3.4; N, 9.5. Found: C, 43.1; H, 3.8; N, 9.7%. UV–Vis (CH_2Cl_2) λ_{max} in nm: 260 (119 000); 289 (sh); 331 (sh); 376 (24 000); 411 (sh). ^{1}H NMR ($CDCl_3$): δ = 2.57, 2.63 (each s, Me); 5.90 (s, CH, dmpz); 6.55–6.82 (m); 7.06 (dd, 7.5, 1.8 Hz); 7.22 (d, 6 Hz); 7.43 (dd, 7 Hz); 7.81 (d, 6 Hz, ^{3}J(Pt–H) = 20 Hz).

2.2.5. Synthesis of [PtCl(PhNCMeNHPh)(ppy)] (7)

To a dichloromethane suspension of [$Pt_2(\mu$-$Cl)_2(ppy)_2$] (157 mg, 0.20 mmol), Ag(PhNCMeNPh) (125 mg, 0.39 mmol) was added and stirred for 3 h. A change in color of the reaction mixture from yellow to dark brown was observed. The solvent was evaporated under vacuum and the residue was extracted with dichloromethane, and passed through a Florisil column. The filtrate was concentrated and hexane (2 mL) was added, the solution on cooling gave yellow crystals (127 mg, 52%). mp: 234 °C. Anal. Calc. for $C_{25}H_{22}ClN_3Pt$: C, 50.4; H, 3.7; N, 7.0. Found: C, 50.0; H, 3.1; N, 6.8%. UV–Vis (CH_2Cl_2) λ_{max} in nm: 255 (31 400); 277 (sh); 325 (sh); 345 (sh); 400 (1700). ^{1}H NMR ($CDCl_3$): δ = 2.09 (s, CMe); 7.10–7.80 (m, Ph, C_6H_4; H-3,4,5 (py)); 9.34 (s, NH); 9.66 (d, 6 Hz, ^{3}J(Pt–H) = 36 Hz, H-4 (py)). $^{195}Pt\{^{1}H\}$ NMR ($CDCl_3$) δ: −3317 ppm.

2.2.6. Synthesis of [$Pt_2Cl_2(\mu$-$Opy)_2(ppy)_2$] (8)

To a suspension of [$Pt_2(\mu$-$Cl)_2(ppy)_2$] (389 mg, 0.50 mmol) in dichloromethane, NaOMe (2.12 mL (0.46 N), 54 mg, 0.99 mmol) was added and stirred for 15 min. To this mixture a methanolic solution of HOpy (106 mg, 1.11 mmol) was added and the whole was further stirred for 2 h. The reaction mixture was dried by evaporating the solvents in vacuo and extracted with dichloromethane by filtering through a G-3 sintered disc. The filtrate was concentrated and few mL of benzene and acetone was added and the solution was kept at 0–5 °C for crystallization to yield orange crystals (121 mg, 25%). mp: 243 °C (dec., darkens above 230 °C). Anal. Calc. for $C_{32}H_{24}Cl_2N_4O_2Pt_2$: C, 40.1; H, 2.5; N, 5.9. Found: C, 39.5; H, 2.3; N, 6.0%. UV–Vis (CH_2Cl_2) λ_{max} in nm: 261 (35 100); 294 (44 500); 326 (sh); 384 (4400); 448 (1400). ^{1}H NMR ($CDCl_3$): δ = 6.44–7.62 (m); 8.08 (d, 6 Hz); 9.05 (d, 6 Hz).

2.2.7. Synthesis of [$Pt_2Cl_2(\mu$-$Spy)_2(ppy)_2$] (9)

To a dichloromethane (10 mL) suspension of [$Pt_2(\mu$-$Cl)_2(ppy)_2$] (143 mg, 0.18 mmol), [$Pb(Spy)_2$] (90 mg, 0.21 mmol) was added and stirred for 3 h. The color of the reaction mixture turned red. This was filtered through a G-3 assembly. The filtrate was concentrated and acetone (1 mL) and hexane (1 mL) were added and the clear solution on cooling at ~5 °C gave red crystals which were separated, washed with benzene/hexane (1:10) mixture and dried (103 mg, 60%), mp: 253 °C. Anal. Calc. for $C_{32}H_{24}Cl_2N_4Pt_2S_2.C_6H_6$: C, 42.7; H, 2.8; N, 5.2; S, 6.0. Found: C, 41.5; H, 2.4; N, 6.0; S, 8.3%. UV–Vis (CH_2Cl_2) λ_{max} in nm: 259 (61 800); 283 (55 300); 352 (20 500); 502 (5300). ^{1}H NMR ($CDCl_3$): δ = 6.48–7.62 (m); 8.17 (d, 6 Hz, ^{3}J(Pt–H) = 30 Hz); 9.54 (d, 6 Hz, ^{3}J(Pt–H) = 18 Hz, H-6(py)).

2.2.8. Synthesis of [$Pt(S_2COEt)(ppy)$] (10)

To a methanolic solution of NaS_2COEt (84 mg, 0.58 mmol), [$Pt_2(\mu$-$Cl)_2(ppy)_2$] (218 mg, 0.28 mmol) was added and stirred for 3 h. The solvents were removed in vacuo and the residue was washed with hexane and extracted with dichloromethane by filtering through a Florisil column. The filtrate was concentrated and few mL of hexane was added, kept at 0–5 °C for crystallization to yield dark yellow crystals (193 mg, 72%) mp: 145 °C. IR: 1713 cm^{-1} (C=O). Anal. Calc. for $C_{14}H_{13}NOPtS_2$: C, 35.7; H, 2.8; N, 3.0; S, 13.6. Found: C, 35.8; H, 2.5; N, 3.2; S, 17.1%. UV–Vis (CH_2Cl_2) λ_{max} in nm: 250 (32 800); 287 (18 200); 329 (sh); 360

(sh); 377 (11 500); 435 (1900). ^{1}H NMR ($CDCl_3$): δ = 1.57 (t, 7.5 Hz, 3H, $OCHCH_3$); 4.75 (q, 7.5 Hz, 2H, OCH_2CH_3); 7.14–8.00 (m); 8.62 (d, 5 Hz, ^3J(Pt–H) = 37 Hz). ^{195}Pt{^{1}H} NMR ($CDCl_3$) δ: −3881 ppm.

2.2.9. Synthesis of [Pt{$S_2P(OPr^i)_2$}(ppy)] (11)

To methanolic solution of $NH_4S_2P(OPr^i)_2$ (188 mg, 0.79 mmol), [$Pt_2(\mu\text{-}Cl)_2(ppy)_2$] (301 mg, 0.39 mmol) was added and stirred 3 h. The solvents were evaporated to dryness and the residue was extracted with dichloromethane. The extract was filtered through a Florisil column and the filtrate was concentrated. Few drops of acetone and hexane were added for crystallization and the mixture was allowed to evaporate slowly. Yellow crystals were obtained (176 mg, 40%) mp: 189 °C. Anal. Calc. for $C_{17}H_{22}NO_2PPtS_2$: C, 36.3; H, 3.9; N, 2.5; S, 11.4. Found: C, 36.3; H, 3.9; N, 2.6; S, 14.1%. UV–Vis (CH_2Cl_2) λ_{max} in nm: 250 (18 300); 287 (12 300); 313 (sh, 5380); 364 (4800); 410 (sh). ^{1}H NMR ($CDCl_3$): δ = 1.42 (d, 6 Hz, 12H, $OCHMe_2$); 4.95 (sept, 6 Hz, 2H, $OCHMe_2$); 7.06–7.90 (m); 8.78 (d, 6 Hz, ^3J(Pt–H) = 45 Hz). ^{31}P{^{1}H}NMR ($CDCl_3$) δ: 96.8 ($^2J(^{195}Pt–^{31}P)$ = 320 Hz). ^{195}Pt{^{1}H} NMR ($CDCl_3$) δ: −3797 (d, $^2J(^{195}Pt–^{31}P)$ = 298 Hz) ppm.

2.3. Crystallography

Intensity data were collected on a Rigaku AFC7S diffractometer fitted with Mo-Kα (λ = 0.71069 Å) radiation so that θ_{max} = 27.5°. The structures were solved by direct methods [22], and refinement [23] was on F^2 using data corrected for absorption correction effects with an empirical procedure [24,25]. The non-hydrogen atoms were refined with anisotropic displacement parameters and fitted with hydrogen atoms in their calculated positions. Molecular structures were drawn using ORTEP [26]. Crystal data and details of collection and refinement are given in Table 1.

3. Results and discussion

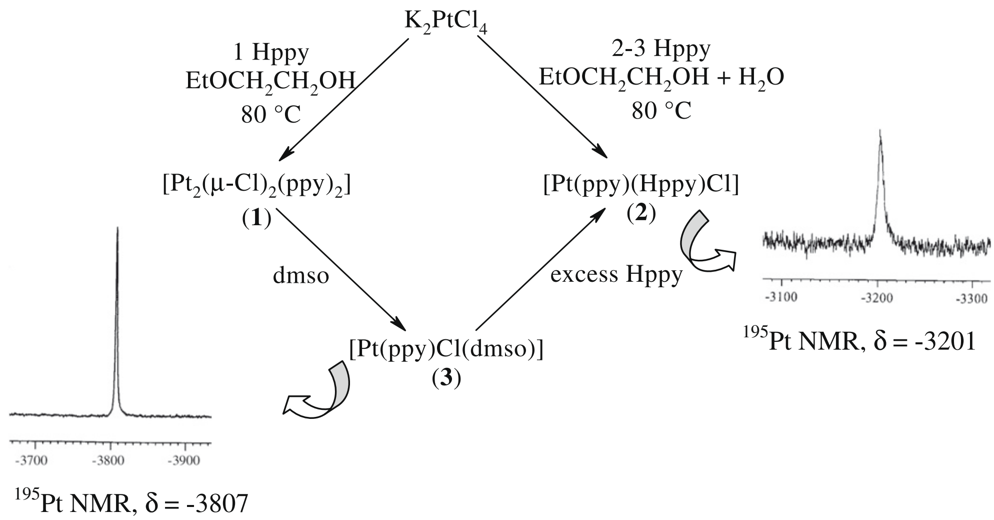
3.1. Synthesis and spectroscopy

The halo-bridged binuclear platinum complexes, [$Pt_2(\mu\text{-}Cl)_2(X)_2L_2$] (X = anionic ligand such as alkyl, aryl, halide; L = neutral donor) are versatile synthons for the preparation of a variety of platinum complexes differing in nuclearity [1]. Accordingly reactions of [$Pt_2(\mu\text{-}Cl)_2(ppy)_2$] with a variety of anionic ligands were conceived for the synthesis of 2-phenylpyridine platinum(II) complexes. The reaction of K_2PtCl_4 with 2-2.5 equivalents of 2-phenylpyridine in a mixture of 2-ethoxyethanol–water (3:1) at 80 °C over a period of 16 h has been reported earlier, without characterizing data, to yield binuclear complex, [$Pt_2(\mu\text{-}Cl)_2(ppy)_2$] (**1**) [17,27] and the resulting product has been used directly in further reactions for the preparation of β-diketonate complexes of the type [Pt(ppy)(β-dik)] [17,20]. It has been shown subsequently that under these conditions [Pt(ppy)(Hppy)Cl] (**2**) is formed [21,28], which and related derivatives, [Pt(Arpy)(HArpy)Cl], have been used for the preparation of β-diketonate complexes, [Pt(C$^\cap$N)(β-dik)] (C$^\cap$N = ppy or Arpy) [21,27,29]. Ford et al. [30], however, obtained **1** by the reaction of [$Bu_4N]_2[PtCl_4$] in ethanol with 1.1 equivalent of Hppy in dichloromethane at room temperature for 5–7 days. Other products, **2** and [$Pt(ppy)Cl_2]^-$ are also formed when 4 equivalents of Hppy was used and the reaction was carried out in MeOH at 50 °C for 12 h [30]. Interestingly the reaction of 2-phenylpyridine with Na_2PdCl_4 is quite facile and yields [$Pd_2(\mu\text{-}Cl)_2(ppy)_2$] [31] which has a *cis* chloro-bridged dimeric structure as revealed by X-ray structural analysis [32].

We have carried out the reaction of 2-phenylpyridine with K_2PtCl_4 under the conditions described earlier [17] and also in 1:1 molar ratio in 2-ethoxyethanol (Scheme 1). In the former case the complex **2**, as reported by Marder et al. [21] and Slugovc et al. [28], was formed while in the latter reaction an insoluble product of composition (from microanalysis) "Pt(ppy)Cl" was isolated in ~65% yield. This complex was soluble in coordinating solvents like

Table 1
Crystallographic and structure refinement data for platinum complexes.

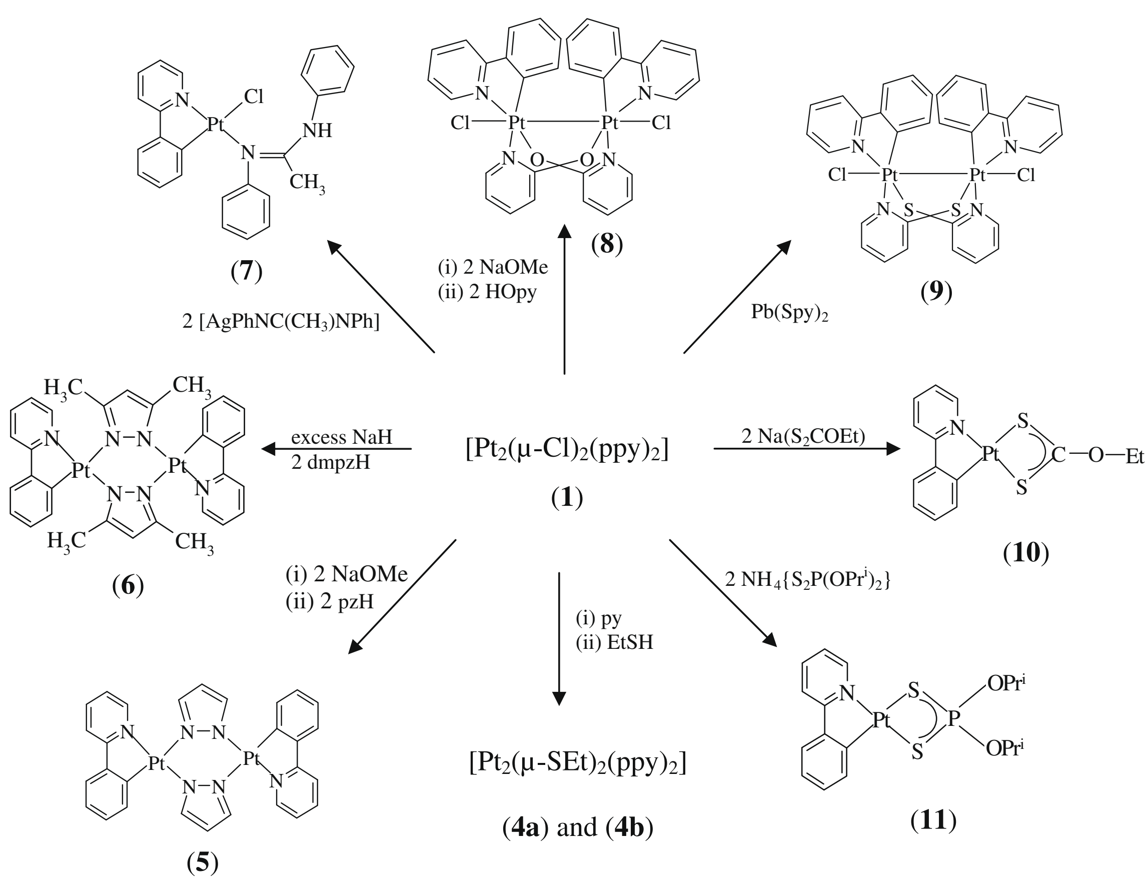
Complex	**5**·$(CH_2Cl_2)_{0.5}$	**6**·$(CH_2Cl_2)_{0.5}$·H_2O	**7**	**8**	**9**·$(C_6H_6)_2$	**10**	**11**
Chemical formula	$C_{28.5}H_{23}ClN_6Pt_2$	$C_{32.5}H_{33}OClN_6Pt_2$	$C_{25}H_{22}ClN_3Pt$	$C_{32}H_{24}Cl_2N_4O_2Pt_2$	$C_{44}H_{36}Cl_2N_4S_2Pt_2$	$C_{14}H_{13}NOPtS_2$	$C_{17}H_{22}NO_2PPtS_2$
Formula weight	875.16	949.25	594.99	957.63	1145.98	470.46	562.59
Crystal size (mm^3)	0.15 × 0.10 × 0.10	0.15 × 0.15 × 0.10	0.40 × 0.20 × 0.10	0.15 × 0.10 × 0.05	0.40 × 0.30 × 0.20	0.50 × 0.20 × 0.50	0.40 × 0.20 × 0.20
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	orthorhombic
Space group	$P2_{1/a}$	$P2_{1/a}$	$P2_{1/n}$	$C2/_c$	$P\bar{1}$	$P2_{1/n}$	P_{nma}
Unit cell dimensions							
a (Å)	23.500(3)	34.423(10)	18.400(3)	15.630(3)	11.694(2)	18.960(6)	9.478(2)
b (Å)	11.651(6)	12.790(6)	7.897(2)	11.341(3)	13.430(3)	5.755(3)	14.5200(15)
c (Å)	19.774(5)	15.160(5)	16.555(3)	16.968(3)	14.200(4)	14.086(5)	14.685(4)
α (°)	90	90	90	90	101.130(18)	90	90
β (°)	102.390(15)	101.49(2)	114.820(12)	102.015(13)	107.377(16)	109.61(3)	90
γ (°)	90	90	90.00(8)	90	110.891(15)	90	90
V (Å^3)	5288(3)	6541(4)	2183.4(8)	2942.0(10)	1873.0(7)	1447.8(10)	2020.9(7)
ρ_{calcd}. (g cm^{-3})	2.198	1.924	1.807	2.162	1.963	2.158	1.855
Z	4	4	4	4	2	4	2
μ (mm^{-1})/F(0 0 0)	10.701/3272	8.662/3592	6.565/1148	9.719/1800	7.751/1058	9.969/888	7.240/1092
Limiting indices	$-17 \leqslant h \leqslant 30$	$-25 \leqslant h \leqslant 44$	$-13 \leqslant h \leqslant 23$	$-11 \leqslant h \leqslant 20$	$-8 \leqslant h \leqslant 15$	$-13 \leqslant h \leqslant 24$	$-6 \leqslant h \leqslant 12$
	$0 \leqslant k \leqslant 15$	$0 \leqslant k \leqslant 16$	$0 \leqslant k \leqslant 10$	$0 \leqslant k \leqslant 14$	$-17 \leqslant k \leqslant 16$	$0 \leqslant k \leqslant 7$	$-10 \leqslant k \leqslant 18$
	$-25 \leqslant l \leqslant 25$	$-19 \leqslant l \leqslant 19$	$-21 \leqslant l \leqslant 19$	$-22 \leqslant l \leqslant 21$	$-18 \leqslant l \leqslant 17$	$-18 \leqslant l \leqslant 17$	$0 \leqslant l \leqslant 19$
Range of data collection (°)	2.55–27.51	2.53–27.50	2.71–27.50	2.66–27.50	2.70–27.51	3.07–27.51	2.56–27.50
Reflections collected/unique	12 109/3770	15 023/4495	5012/3088	3387/2326	8598/5855	3333/2482	2414/1234
Data/restraints/parameters	12 109/0/262	15 023/0/198	5012/0/272	3387/0/190	8598/0/460	3333/0/173	2414/0/119
Final R_1, wR_2 indices	0.0848/0.2355	0.0734/0.1791	0.0639/0.2020	0.0353/0.0790	0.0484/0.1548	0.0257/0.0647	0.0492/0.1371
R_1, wR_2 (all data)	0.3156/0.1645	0.3100/0.1427	0.1230/0.1657	0.0777/0.0719	0.1413/0.0869	0.0647/0.0558	0.1402/0.1099
Goodness of fit (GOF) on F^2	0.907	0.81	1.025	1.014	1.001	1.087	0.988



Scheme 1.

dmso and gave a complex of composition [Pt(ppy)Cl(dmso)] (**3**) which was structurally characterized (see Supplementary material). The cleavage of chloro-bridged binuclear platinum complexes with dmso to yield mononuclear complexes is well documented [33]. The ^{195}Pt NMR spectrum of **3** in dmso exhibited a single resonance at δ −3807 ppm. When a dmso solution of **3** was treated with an excess of 2-phenylpyridine in NMR tube, a new ^{195}Pt resonance appeared at δ −3201 ppm attributable to **2**. Based on this, the insoluble complex formed in 1:1 reaction can be considered as binuclear complex $[Pt_2(\mu\text{-}Cl)_2(ppy)_2]$ (**1**). The reaction of K_2PtCl_4 with 2 or more equivalents of 2-phenylpyridine appears to yield initially **1** which undergoes bridge cleavage reaction with the excess of 2-phenylpyridine to afford **2**.

Various complexes synthesized using **1** are shown in Scheme 2. The reaction of **1** with an excess of ethylmercaptan in the presence of pyridine as HCl scavenger in dichloromethane afforded bis(thiolato)-bridged complex, $[Pt_2(\mu\text{-}SEt)_2(ppy)_2]$ (**4**). Interestingly attempts to prepare bis(thiolato)-bridged palladium complexes



Scheme 2.

containing C∩N type ligands led to the isolation of mixed chloro/mercapto bridged complexes, $[Pd_2(\mu\text{-}Cl)(\mu\text{-}SR)(C^\cap N)_2]$ [34–37]. However, heavier organochalcogenolate ligands readily give bis(organochalcogenolate) complexes, $[Pd_2(\mu\text{-}EAr)_2(C^\cap N)_2]$ (E = Se or Te) [34]. The ^{1}H NMR spectrum of **4** in $CDCl_3$ exhibited two sets of resonances attributable to *cis* and *trans* isomers. The *trans* isomer displayed a triplet and a quartet for CH_3 and CH_2 protons of magnetically equivalent two SEt groups. For the *cis* isomer two sets of triplets and quartets were observed for two non-equivalent SEt groups, one trans to metalated carbon and another trans to nitrogen donor atom of ppy. Platinum complexes derived from metalated phosphine ligand and bridging organochalcogenolate ligands have been isolated as a mixture of *cis* and *trans* isomers [38,39].

The reaction of **1** with pyrazole and 3,5-dimethylpyrazole in the presence of a base gave pyrazolato-bridged derivatives, $[Pt_2(\mu\text{-}N^\cap N)_2(ppy)_2]$ (N∩N = pz (**5**); dmpz (**6**)]. Treatment of **1** with silver salt of 1,3-diphenylacetamidine gave a mononuclear complex, [PtCl(PhNCMeNHPh)(ppy)] (**7**) rather than the acetamidinato–bridged complex. The **7** appeared to be formed by the reaction of moisture on acetamidine complex. The reactions of small bite three-atom anionic ligand, pyOH and pySH, with **1** gave after processing binuclear platinum(III) complexes, $[Pt_2Cl_2(\mu\text{-}Opy)_2(ppy)_2]$ (**8**) and $[Pt_2Cl_2(\mu\text{-}Spy)_2(ppy)_2]$ (**9**), as isolable products. These ligands have been known to give binuclear platinum complexes with short metal-metal contacts which undergo facile oxidation leading to the formation of platinum(III) complexes [40]. For example, the complex, $[Pt(Spy)_2]_2$ is readily oxidized in halogenated solvents (e.g. $CHCl_3$) to give $[Pt_2X_2(Spy)_4]$ [41]. The complexes **8** and **9** represent rare examples of orthometalated platinum complexes in higher oxidation state (>2) of platinum. Recently orthometalated palladium(III) and platinum(IV) complexes have been described [42–44]. The palladium(III) complex $[Pd_2X_2(\mu\text{-}OAc)_2(benz)_2]$ (benz = metalated benzoquinoline) undergo bimetallic reductive elimination of halogenated benzoquinoline [44]. The reaction of **1** with large bite three-atom anionic ligands, such as ethylxanthate and diisopropyldithiophosphate yielded mononuclear complexes, $[Pt(S^\cap S)(ppy)]$ ($S^\cap S$ = S_2COEt (**10**); $S_2P\{OPr^i\}_2$ (**11**)) in which the dithiolate ligand is chelated.

The mononuclear complexes **2**, **3** and **7** adopt a configuration in which nitrogen atom of the chelating ppy ligand is *trans* to the donor atom of the incoming ligand. A configuration with the N atom of the ppy *cis* to neutral donor would be unfavorable as it would be expected to isomerize via a dissociative mechanism [45].

The ^{1}H NMR spectra of these complexes displayed expected resonances. The CH-6 proton of pyridine ring of the chelating ppy ligand appeared as a doublet in the range 7.81–9.66 ppm with $^3J(^{195}Pt–^1H)$ of 18–37 Hz. The ^{195}Pt NMR of **2**, **3**, **7**, **10**, **11** displayed single resonances in the region δ −3201 to −3881 ppm. The ^{195}Pt signal for **11** appeared as a doublet due to coupling with a phosphorus nucleus ($^2J(^{195}Pt–^{31}P)$ = 298 Hz) of the dithiophosphate ligand. The ^{31}P NMR spectrum of **11** displayed a singlet at δ 96.8 ppm with $^2J(^{195}Pt–^{31}P)$ of 320 Hz, indicative of chelating dithiophosphate ligand [46,47]. The magnitude of $^2J(^{195}Pt–^{31}P)$ is in accord with dithiophosphate complexes of platinum(II) [46].

These complexes vary in color from pale -yellow, -orange to -red. Absorption spectra of these complexes in dichloromethane showed bands assignable to $\pi–\pi^*$ and MLCT transitions from metalated ppy ligand in the region 255–400 nm. The lower energy weaker absorption bands may be assigned to metal-to-ligand charge transfer transition. The absorption band in **2** at 400 nm (lit. 402 nm [19] due to MLCT) is blue shifted in dmso complex **3** (372 nm). It is worth noting that when nitrogen ligands whether in the terminal position (as in **7**) or in bridging mode (e.g. **5** and **6**) are substituted with sulfur donors in either situation (e.g. **3** in dmso complex and **4** in thiolato bridge) the MLCT band is blue shifted and appears at ~370 nm. Similarly the absorptions in dithiolate complexes (**10** and **11**) are blue shifted with respect to the absorption band for [Pt(acac)(ppy)] [17,20]. The binuclear complexes (**5**, **6**, **8**, **9**) with shorter Pt–Pt separation exhibited an additional weak band of lower energy (406–502 nm) which may be assigned to metal–metal-to-ligand charge transfer (MMLCT) transition. This band is red shifted with decreasing Pt–Pt separation. Preliminary work on photoluminescence revealed that these complexes, except $[Pt_2(\mu\text{-}SEt)_2(ppy)_2]$, are emissive in solution. A detailed study on photoluminescence properties of these complexes will be published separately.

3.2. Crystal structures

Molecular structures of these complexes have been established unequivocally by single crystal X-ray diffraction analyses. ORTEP drawings are shown in Figs. 1-7 and selected interatomic parameters for **8** and **9** are given in Tables 2 and 3. The metalated 2-phenylpyridine ligands, in general, have a planar arrangement around distorted square planar platinum atom. The Pt–C and Pt–N distances involving metalated 2-phenylpyridine lie in the ranges 1.958–2.074 and 1.963–2.148 Å, respectively, while the N–Pt–C angles vary between 78.6 and 82.3°. The acute N–Pt–C angle is characteristic of orthometalated five membered C∩N ligands in transition metal complexes. The Pt–C and Pt–N distances and N–Pt–C angle in the complexes reported here are well within the range reported in orthometalated 2-phenylpyridine complexes of platinum such as [PtCl(ppy)(Hppy)] [30], [Pt(ppy)(PhCOCHCOPh)] [20] and $[Pt(ppy)\{(Me_2pz)_2BH_2\}]$ [17].

Table 2
Selected bond lengths (Å) and angles (°) for $[Pt_2Cl_2(\mu\text{-}Opy)_2(ppy)_2]$ (**8**).

Pt(1)–Cl(1)	2.454(2)	Pt(1)–C(12)	1.988(7)
Pt(1)–N(1)	2.050(6)	Pt(1)–Pt(1)^i	2.5681(7)
Pt(1)–O(1)	2.134(5)	C(1)–O(1)	1.280(8)
Pt(1)–N(2)	2.016(6)	C(1)–N(1)	1.375(9)
Cl(1)–Pt(1)–Pt(1)^i	173.63(4)	N(1)–Pt(1)–C(12)	94.0(3)
Cl(1)–Pt(1)–Cl(2)	88.6(2)	O(1)–Pt(1)–Pt(1)^i	82.70(14)
Cl(1)–Pt(1)–N(2)	84.61(18)	O(1)–Pt(1)–N(2)	95.4(2)
Cl(1)–Pt(1)–O(1)	91.03(15)	O(1)–Pt(1)–Cl(12)	177.1(3)
Cl(1)–Pt(1)–N(1)	96.71(17)	N(2)–Pt(1)–Pt(1)^i	94.89(17)
N(1)–Pt(1)–O(1)	88.9(2)	N(2)–Pt(1)–C(12)	81.6(3)
N(1)–Pt(1)–Pt(1)^i	84.29(17)	C(12)–Pt(1)–Pt(1)^i	97.6(2)
N(1)–Pt(1)–N(2)	175.4(2)		

Table 3
Selected bond lengths (Å) and angles (°) for [Pt2Cl2(μ-Spy)2(ppy)2]·(C6H6)2 (9·(C6H6)2).

Pt(1)–Cl(1)	2.487(3)	Pt(2)–Cl(2)	2.475(4)
Pt(1)–S(1)	2.305(3)	Pt(2)–S(2)	2.312(3)
Pt(1)–N(2)	2.168(7)	Pt(2)–N(1)	2.173(7)
Pt(1)–N(3)	2.024(9)	Pt(2)–N(4)	2.015(9)
Pt(1)–C(17)	2.069(7)	Pt(2)–C(28)	2.067(8)
Pt(1)–Pt(2)	2.6253(7)		
Cl(1)–Pt(1)–Pt(2)	176.34(7)	Cl(2)–Pt(2)–Pt(1)	176.08(8)
Cl(1)–Pt(1)–N(2)	92.0(2)	Cl(2)–Pt(2)–N(1)	88.9(2)
Cl(1)–Pt(1)–S(1)	89.87(11)	Cl(2)–Pt(2)–S(2)	93.80(11)
Cl(1)–Pt(1)–N(3)	85.8(3)	Cl(2)–Pt(2)–N(4)	89.2(3)
Cl(1)–Pt(1)–C(17)	88.3(2)	Cl(2)–Pt(2)–C(28)	84.8(2)
N(2)–Pt(1)–Pt(2)	86.5(2)	N(1)–Pt(2)–Pt(1)	87.2(2)
N(2)–Pt(1)–S(1)	86.4(2)	N(1)–Pt(2)–S(2)	86.3(2)
N(2)–Pt(1)–N(3)	177.1(3)	N(1)–Pt(2)–N(4)	177.4(3)
N(2)–Pt(1)–C(17)	96.8(3)	N(1)–Pt(2)–C(28)	97.6(3)
S(1)–Pt(1)–Pt(2)	86.71(8)	S(2)–Pt(2)–Pt(1)	86.63(7)
S(1)–Pt(1)–N(3)	95.6(3)	S(2)–Pt(2)–N(4)	95.6(3)
S(1)–Pt(1)–C(17)	176.3(2)	S(2)–Pt(2)–C(28)	175.8(2)
N(3)–Pt(1)–Pt(2)	95.8(3)	N(4)–Pt(2)–Pt(1)	94.6(2)
N(3)–Pt(1)–C(17)	81.1(3)	N(4)–Pt(2)–C(28)	80.4(4)
C(17)–Pt(1)–Pt(2)	95.2(2)	C(28)–Pt(2)–Pt(1)	95.1(2)

The structural features of [PtCl(ppy)(Hppy)] [30] and [PtCl(dmso)(ppy)] [48] (see Supplementary material) are in accordance with the structural parameters reported earlier.

The molecular structure of [PtCl(ppy)(PhNCMeNHPh)] is shown in Fig. 3. The amidine ligand is coordinated to platinum through C=N and is *trans* to the nitrogen atom of the metalated 2-ppy ligand. The two Pt–N distances are comparable and are in accordance with Pt–N bond length reported in other platinum complexes, such as [$PtCl_2$(bipy)] [29]. The N–C–N angle in amidine (115.0(12)°) is reduced markedly from the ideal value of 120°.

The pyrazolato–bridged complexes, [Pt_2(μ-pz)$_2$(ppy)$_2$] and [Pt_2(μ-dmpz)$_2$(ppy)$_2$], (Figs. 1 and 2, respectively) comprise of two "Pt(ppy)" fragments which are held together by exo-bidentate pyrazolate ligands. The six-membered "Pt_2N_4" ring has a boat conformation with the platinum atoms at the vertexes of the boat. Similar boat conformation has been reported in [Pt_2Cl_2(μ-dmpz)$_2$($PMePh_2$)$_2$] [49], [Pt_2(μ-dmpz)$_2$($P^{\cap}C$)$_2$] [50] and [Pt_2(μ-pz)$_2$(thpy)$_2$] [29]. The two pyrazolato-ligands are planar within experimental error and the average dihedral angles between the two planes are 100.4° and 98.98°, respectively. The molecules adopt a sym-*trans* configuration. Both sym-*trans* (e.g. [Pt_2(μ-pz)$_2$(thpy)$_2$]

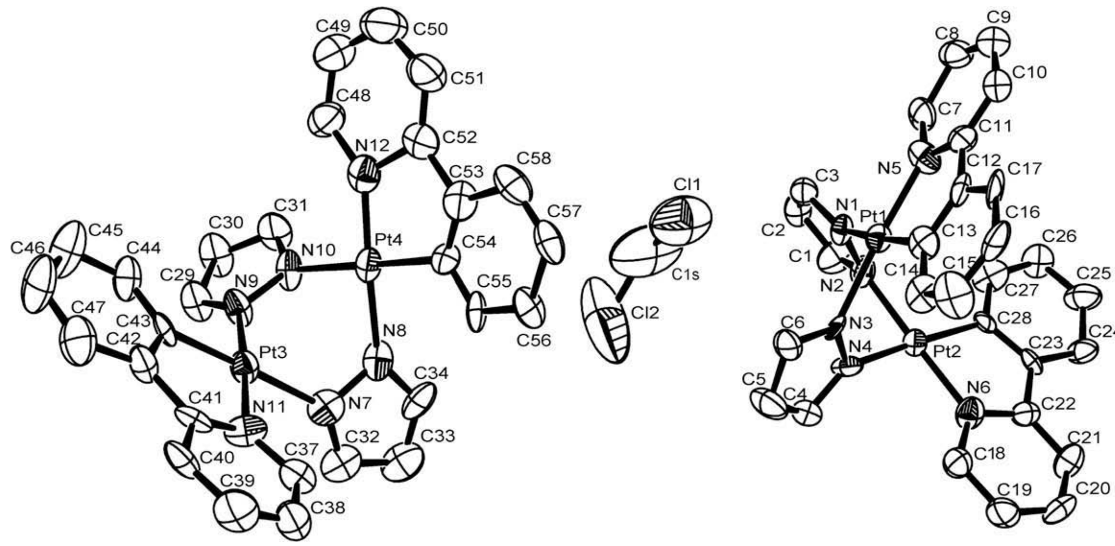


Fig. 1. ORTEP drawing with crystallographic numbering scheme for [Pt_2(μ-pz)$_2$(ppy)$_2$]·(CH_2Cl_2)0.5 (**5**·(CH_2Cl_2)$_{0.5}$) (ellipsoids drawn with 50% probability). Selected bond lengths (Å) and angles (°): Pt(1)–N(1) 2.11(2), Pt(1)–N(3) 2.09(2), Pt(3)–N(7) 2.04(2), Pt(3)–N(9) 2.04(2), Pt(2)–N(2) 2.02(2), Pt(4)–N(10) 2.08(2), Pt(2)–N(4) 2.01(2), Pt(4)–N(8) 2.00(3), Pt(1)–Pt(2) 3.289, Pt(3)–Pt(4) 3.289, N(1)–Pt(1)–N(3) 86.3(8), N(9)–Pt(3)–N(7) 87.1(9), N(2)–Pt(2)–N(4) 87.1(8), N(10)–Pt(4)-N(8) 84.8(9).

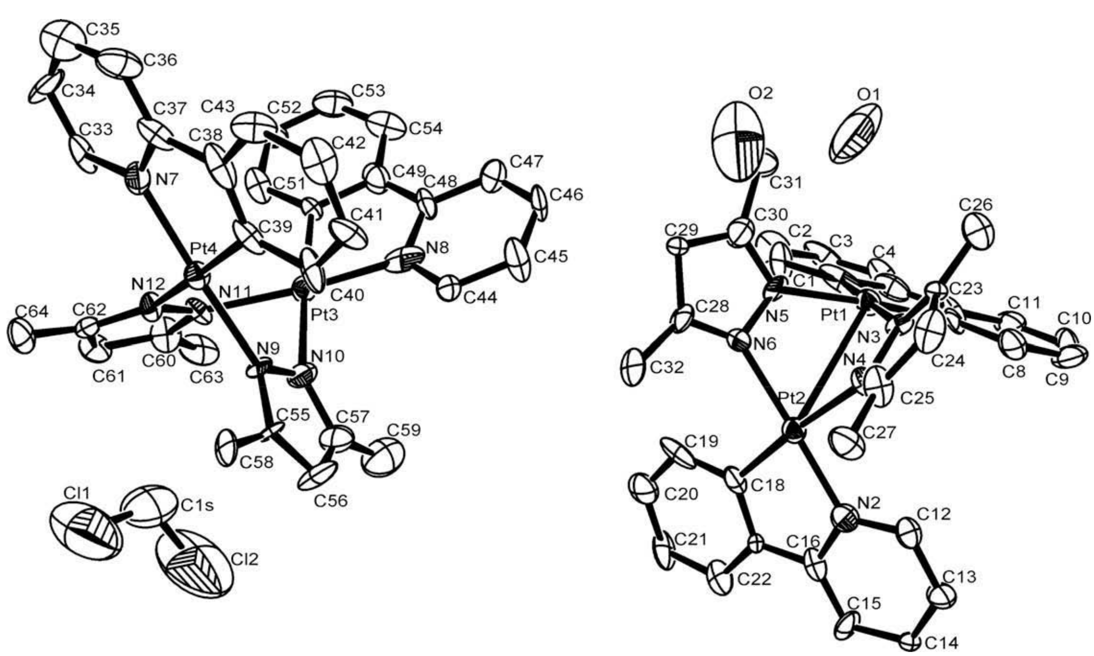


Fig. 2. ORTEP drawing with crystallographic numbering scheme for [Pt_2(μ-dmpz)$_2$(ppy)$_2$]·(CH_2Cl_2)$_{0.5}$·H_2O (**6**·(CH_2Cl_2)$_{0.5}$·H_2O), (ellipsoids drawn with 50% probability). Selected bond lengths (Å) and angles (°)**:** Pt(3)–N(10) 2.076(15), Pt(1)–N(3) 2.050(14), Pt(3)–N(11) 2.063(13), Pt(1)–N(5) 2.005(16), Pt(4)–N(12) 2.095(14), Pt(2)–N(4) 2.078(14), Pt(2)–N(6) 2.070(15), Pt(4)–N(9) 1.997(13), Pt(2)–Pt(1) 3.1904(13), Pt(4)–Pt(3) 3.2029(13), N(10)–Pt(3)–N(11) 84.9(6), N(3)–Pt(1)–N(5) 85.5(6), N(4)–Pt(2)–N(6) 85.3(6), N(12)–Pt(4)–N(9) 88.0(6).

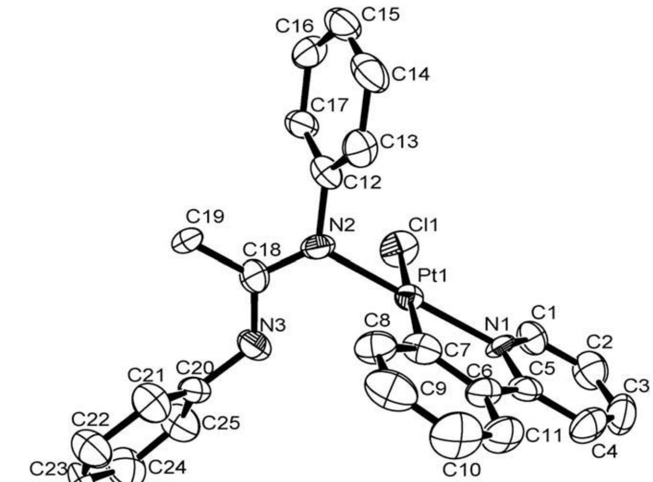


Fig. 3. ORTEP drawing with crystallographic numbering scheme for [Pt(ppy)(PhNHCMeNPh)Cl] (**7**) (ellipsoids drawn with 50% probability). Selected bond lengths (Å) and angles (°): Pt(1)–Cl(1) 2.405(3), Pt(1)–C(7) 1.958(13), Pt(1)–N(1) 2.038(10), N(2)–C(18) 1.326(19), Pt(1)–N(2) 2.036(11), N(3)–C(18) 1.348(18), Cl(1)–Pt(1)–N(1) 95.7(3), N(1)–Pt(1)–N(2) 176.3(5), Cl(1)–Pt(1)–N(2) 87.5(4), Pt(1)–N(2)–C(18) 125.5(9), N(2)–C(18)–N(3) 115.0(12).

[29], $[Pt_2(\mu\text{-}3\text{-}Me,5\text{-}Bu^tpz)_2\{(2,4\text{-}F_2C_6H_2)py\}_2]$ [51] and sym-cis (e.g. $[Pt_2(\mu\text{-}N^\cap N)_2\{(2,4\text{-}F_2C_6H_2)py\}_2]$ ($N^\cap N$ = pz, dmpz, $Bu^t{}_2pz$)) [51] have been reported for metalated arylpyridine platinum complexes containing pyrazolate-bridges. The two-bridging pyrazolate ligands form disparate Pt–N bonds reflecting the different *trans* influence of the C-(phenyl) and N (pyridyl) donor atoms of ppy. The shorter Pt–N distances have the N atoms trans to N of ppy while longer Pt–N bond lengths have the N(pz) *trans* C (phenyl) atom. The Pt···Pt spacings are 3.289 (for pz) and av. 3.196 (for dmpz) Å. The Pt···Pt separations in various pyrazolato-bridged complexes are 3.170(1) Å $[Pt_2Cl_2(\mu\text{-}dmpz)_2(PMePh_2)_2]$ [49]; 3.432(1) Å $[Pt_2(\mu\text{-}pz)_2(thpy)_2]$ [29]; 2.8343–3.3763Å $[Pt_2(\mu\text{-}N^\cap N)_2\{(2,4\text{-}F_2C_6H_2)py\}_2]$ [51]. The Pt···Pt separation decreases by substituting bulky groups at 3- and 5-positions of the bridging pyrazolate ligand [51]. There are weak π–π interactions between the ppy groups of two molecules. The two boat-shaped molecules are entangled in each other.

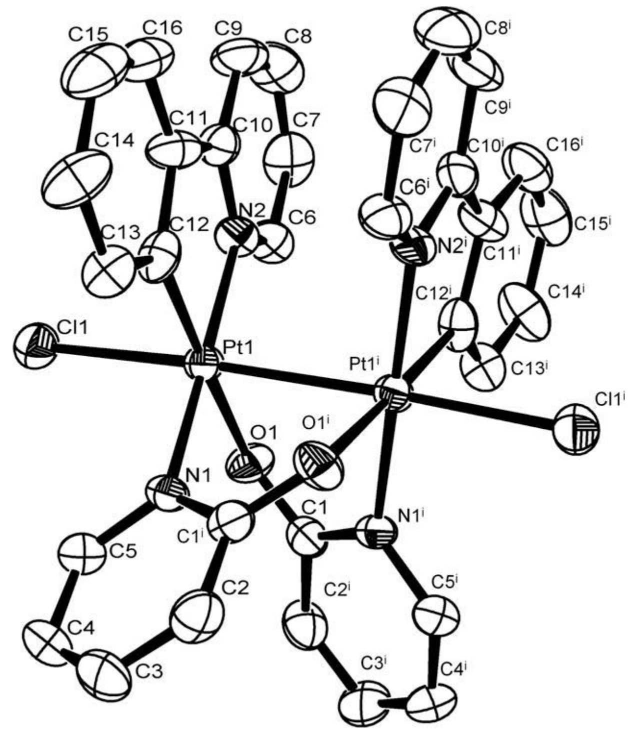


Fig. 4. ORTEP drawing with crystallographic numbering scheme for $[Pt_2Cl_2(\mu\text{-}Opy)_2(ppy)_2]$ (**8**) (ellipsoids drawn with 50% probability).

The complexes $[Pt_2Cl_2(\mu\text{-}Opy)_2(ppy)_2]$ and $[Pt_2Cl_2(\mu\text{-}Spy)_2(ppy)_2]$ (Figs. 4 and 5, respectively) have similar geometries containing two platinum atoms bridged by two pyE (E = O or S) ligands in a head-to-tail fashion and overall configuration can be compared

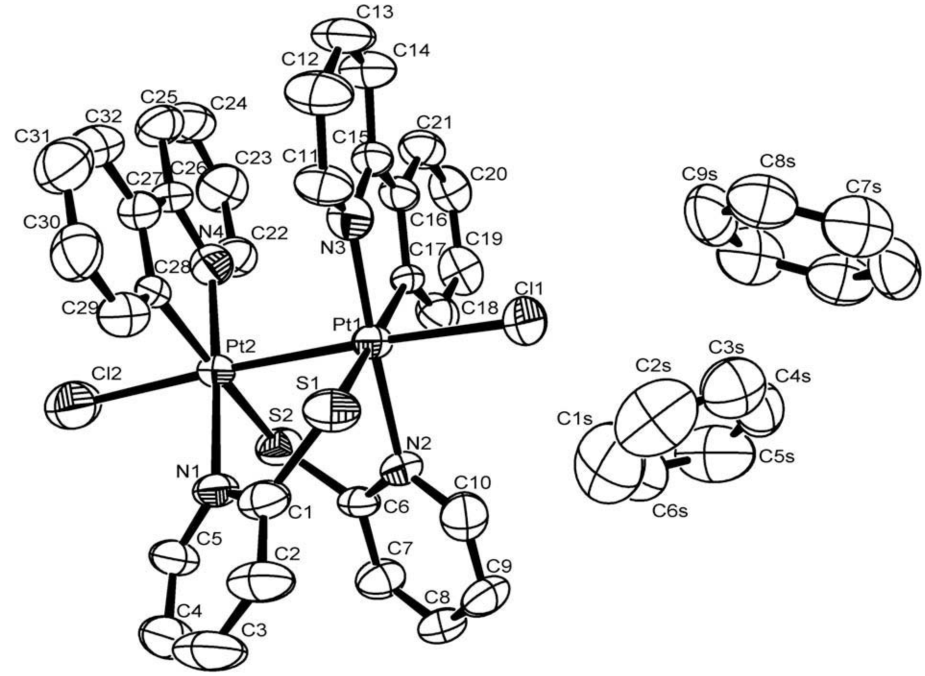


Fig. 5. ORTEP drawing with crystallographic numbering scheme for $[Pt_2Cl_2(\mu\text{-}Spy)_2(ppy)_2]\cdot(C_6H_6)_2$ ($\mathbf{9}\cdot(C_6H_6)_2$) (ellipsoids drawn with 50% probability).

with $[Pt_2Cl_2(Opy)_2(en)_2]^{2+}$ (en = $H_2NCH_2CH_2NH_2$) [52,53]. Each platinum atom adopts an octahedral configuration defined by chelating ppy ligand, E and N atoms of pyE ligands, a chloride and a Pt–Pt bond. The oxygen/sulfur atom of Epy ligand is *trans* to the C-atom of the metalated ppy. The platinum atom coordination planes are deviated with the twist angles (defined by the torsion angle E–Pt–Pt–N) of 26.57° and 33.21° from the ideal eclipsed configuration. The ppy rings are inclined to each other at an angle of 14.81° and 13.89° in **8** and **9**, respectively. The Pt–Cl distances (av. 2.454 Å in Opy and av. 2.481 Å in Spy) can be compared with those found in Pt(III) complexes (e.g. $[Pt_2Cl_2(4\text{-}MepyS)_4]$, Pt–Cl = av. 2.451 Å) [54]. The Pt–Pt distances 2.5681(7) Å (in Opy) can be compared to the reported value $[Pt_2XY(Opy)_2(NH_3)_4]^{2+}$ (av. 2.575 Å) [55], whereas 2.6253(7) Å (in pyS) is slightly longer than reported for $[Pt_2Cl_2(Spy)_4]$ (2.532(1) Å) [40]. The Pt–Pt distance in platinum(III) complexes varies between 2.39 and 2.78 Å, being shorter with smaller bite ligands [41].

The crystal structure of $[Pt(S_2COEt)(ppy)]$ (Fig. 6) consists of discrete monomeric molecules. The geometry around platinum is distorted square planar and is defined by the N and C atoms of the metalated 2-phenylpyridine and two sulfur atoms of slightly asymmetrically chelated xanthate ligand. The latter adopts its characteristic geometry of chelated xanthate ligand in metal complexes [56]. The strain imposed by the four-membered PtS_2C ring is reflected in the S–Pt–S angle which is compressed to 74.28(6)° while the adjacent angles C7–Pt1–S2 and N1–Pt1–S1 are opened to 101.79(19)° and 102.82(15)°, respectively. The Pt–S distance trans to C-(phenyl) is longer than the one *trans* to nitrogen (pyridyl) owing to their different trans influences. The Pt–S distances are well within the range reported for the dithiolato complexes, e.g. $[PtMe\{S_2P(OPr^i)_2\}(AsPh_3)]$ (Pt–S = 2.341(2), 2.434(2) Å) [46], $[PtBu^i\{S_2CNMe_2\}(Pc\text{-}Hx_3)]$ (Pt–S = 2.404(2), 2.412(3)) [57]. The two C–S distances are similar (1.684(6) and 1.698(6) Å) and are intermediate between double (1.62 Å) and single bond (1.81 Å) values indicating delocalization of double bond over OCS_2^- moiety.

The crystal structure of $[Pt\{S_2P(OPr^i)_2\}(ppy)]$ (Fig. 7) shows that the square planar platinum is coordinated by C and N atoms of ppy ligand and the two S atoms of symmetrically chelated dithiophosphate ligand. The molecule has a mirror plane bisecting Pt and P atoms, thus C and N atoms of ppy are indistinguishable. Unlike the xanthate complex, the dithiophosphate is symmetrically chelated as the two Pt–S distances (2.371(3) Å) are same and are in accord with the literature values (e.g. $[Pt\{S_2P(OEt)Ph\}_2]$ (Pt–S = 2.333(3) and 2.341(3) Å) [58] and $[Pt\{S_2P(OEt)_2\}_2(PPh_3)]$ (Pt–S = 2.325(10)–2.388(12) Å) [47]. The Pt–S distances (2.003(4) Å) are similar and are intermediate between single (2.09 Å) and double bond (1.94 Å) values indicating symmetrically delocalized P–S π bond. The acute S–Pt–S angle (82.8°) is within the range (~83°) of chelating dithiophosphate ligand ($[Pt\{S_2P(OEt)_2\}_2(PPh_3)]$ (S–Pt–S = 82.7(3)°) [47] and $[PtMe\{S_2P(OPr^i)_2\}(AsPh_3)]$ (S–Pt–S = 83.10(7)° [54].

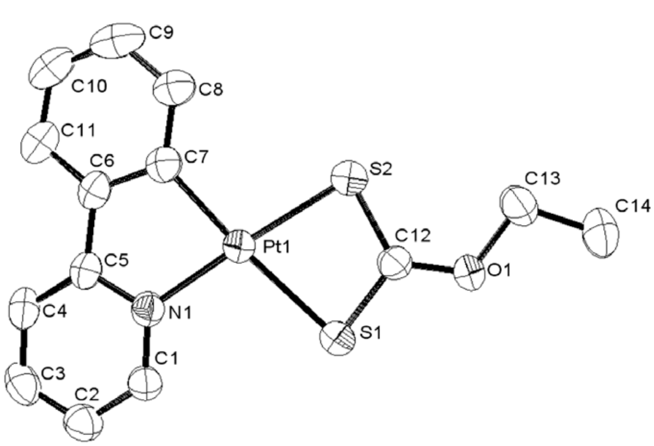


Fig. 6. ORTEP drawing with crystallographic numbering scheme for $[Pt(S_2COEt)(ppy)]$ (**10**) (ellipsoids drawn with 50% probability). Selected bond lengths (Å) and angles (°): Pt(1)–S(1) 2.4018(19), S(1)–C(12) 1.684(6), Pt(1)–S(2) 2.3106(18), S(2)–C(12) 1.698(6), Pt(1)–N(1) 2.018(5), C(12)–O(1) 1.315(7), Pt(1)–C(7) 2.008(6), S(1)–Pt(1)–S(2) 74.28(6), S(2)–Pt(1)–C(7) 101.79(19), Pt(1)–S(1)–C(12) 84.2(2), S(1)–C(12)–S(2) 114.6(4), Pt(1)–S(2)–C(12) 86.9(2), S(1)–C(12)–O(1) 119.7(4), S(2)–C(12)–O(1) 125.7(5), S(1)–Pt(1)–N(1) 102.82(15), C(7)–Pt(1)–N(1) 81.1(2).

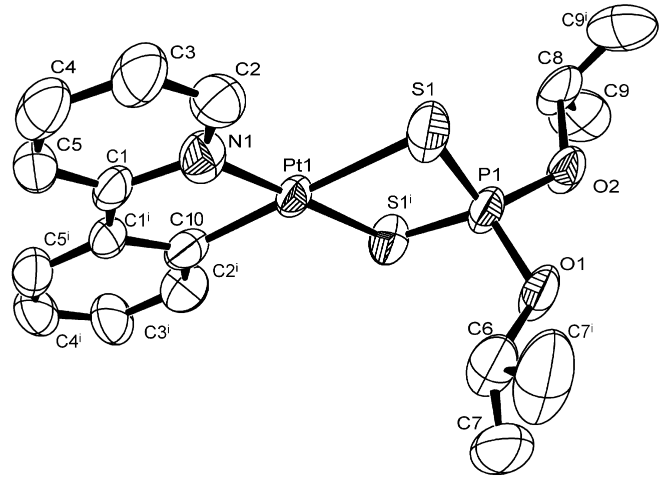


Fig. 7. ORTEP drawing with crystallographic numbering scheme for $[Pt(S_2P\{OPr^i\}_2)(ppy)]$ (**11**) ($N1^i$ has been changed to C10 in the figure) (ellipsoids drawn with 50% probability). Selected bond lengths (Å) and angles (°): Pt(1)–S(1) 2.371(3), P(1)–S(1) 2.003(4), Pt(1)–S(1)^i 2.371(3), P(1)–S(1)^i 2.003(4), Pt(1)–N(1) 2.020(9), P(1)–O(1) 1.569(10), Pt(1)–C(10) 2.020(9), P(1)–O(2) 1.570(9), S(1)–Pt(1)–S(1)^i 82.80(17), S(1)–P(1)–S(1)^i 103.0(2), N(1)–Pt(1)–C(10) 82.1(5).

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Appendix A. Supplementary material

CCDC 737106, 737107, 737108, 737109, 737110, 737111, 737112, 737113 and 737114 contain the supplementary crystallographic data for complexes **5**, **6**, **7**, **8**, **9**, **10**, **11**, **2** and **3**, respectively 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.jorganchem.2010.01.035.

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