

Synthesis and characterization of heterobimetallic complexes with pyridyl selenolato ligands. Crystal structure of $[\{Pt(C_5H_4N)(SeC_5H_4N)(dppp)\}ZnCl_2]$

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Abstract

Reactions of $[Pt(SeC_5H_4N)_2(P\cap P)]$ with $M(OAc)_2 \cdot 2H_2O/MX_2$ ($P\cap P = dppm, dppp$; $M = Zn, Cd, Hg, Cu$; $X = Cl$) resulted various products depend upon the nature of the phosphine. In case of $dppm$, reaction between $[Pt(SeC_5H_4N)_2(dppm)]$ and $M(OAc)_2 \cdot 2H_2O/MX_2$ ($M = Zn, Cd, Hg$) afforded an exchange product of composition $[PtCl_2(dppm)]$. Similarly, the reaction with ‘ $dppp$ ’ analog yielded an adduct $[\{Pt(SeC_5H_4N)_2(dppp)\}MX_2]$ ($M = Cd, Hg, Cu$; $X = Cl, OAc$). Whereas, reaction with $Zn(OAc)_2$, on extraction with dichloromethane resulted the product with the loss of one selenium atom of composition $[\{Pt(C_5H_4N)(SeC_5H_4N)(dppp)\}ZnCl_2]$. These complexes were characterized by elemental analyses and NMR (1H , ^{31}P , ^{77}Se , ^{195}Pt) spectroscopy. The molecular structure of $[\{Pt(C_5H_4N)(SeC_5H_4N)(dppp)\}ZnCl_2]$ was established by single crystal X-ray diffraction analyses.

Keywords: Platinum, Selenolate, NMR, X-ray, Phosphines.

1. Introduction

The nature of metallophilic bonding (i.e. attractive interaction between closed shell transition metals) has been drawn considerable interest for quite some time. Due to rich coordination reactivity and structural diversity [1-5], it finds proven application in the field of material science [6-8] and design of luminescent compounds [9, 10]. There is the range of strategies applied for the development of various metallophilic ligands, part of the attention has been focused towards d^8 metal complexes that have a variable chalcogen and metal atom in their inner core. The easiest type of system consists of two chalcogen and two metal centers (M_2S_2).

In 1971, Ugo et. al. reported a powerful metallophilic binuclear complex $[Pt_2(\mu-S)_2(PPh_3)_4]$ [11]. These metalloligands, $[Pt_2(\mu-S)_2(P-P)_2]$ [$P-P = 2PPh_3, 2dppy, dppp, dppf, 2PMe_2Ph, dppe$] show powerful Lewis basicity towards d- and f- block elements [12-15]. Renewed interest in the development of metallophilic bonds through the metal chalcogen core, has been shown by V. W.-W. Yam et. al. They have performed a reaction between $[Pt_2(\mu-E)_2(dppy)_4]$ ($dppy = 2$ diphenylphosphineopyridine) ($E = S, Se$) and $[M_2(dppm)]$, which yielded polynuclear complexes $[Pt_2(dppy)_4(\mu_3-E)_2M_2(dppm)]^{2+}$ ($M = Cu, Ag, Au$) [15]. They have also performed the same reaction with $[M(CH_3CN)_4]^+$ ($M = Cu, Ag$) and isolated a tetranuclear d^{10} copper(I) and silver(I) clusters containing a μ_4 -sulfido moiety which all exhibits rich photochemical and physical properties [16-18]. Thus, the Lewis basic core $\{Pt_2(\mu-E)_2\}$ ($E = S, Se$) can be combined with Lewis acidic metal complexes to give mixed-metal materials as well as multinuclear homo-platinum complexes [15]. Despite growing interest in the Pt_2S_2 core as a metallophilic ligand still the heavier analog like $Pt_2Se_2, PtSe_2$ remain uncharted, even those which have proven better nucleophilic behavior [19, 20] and luminescence property [21, 22].

Thus fully characterized heterometallic complexes bridged with heavier chalcogen ligands for example selenolato and telluroolato ligands are comparatively very few in number. Therefore, in this work, we have described the synthesis and characterization of some new heterometallic complexes derived from $[\text{Pt}(\text{SeC}_5\text{H}_4\text{N})_2(\text{P}\cap\text{P})]$ ($\text{P}\cap\text{P} = \text{dppm}, \text{dppp}$) (from substitution reaction between $[\text{PtCl}_2(\text{P}\cap\text{P})]$ with two mole of sodium salt of pyridyl selenolate) and $\text{M}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Zn}, \text{Cd}, \text{Hg}, \text{Cu}$). The result of the work is reported as here in.

2. Experimental

2.1 Materials and methods

The compounds $[\text{PtCl}_2(\text{P}\cap\text{P})]$ [$\text{P}\cap\text{P} = \text{dppm}$ (bis(diphenylphosphino)methane), dppe , dppp (1,3-bis(diphenylphosphino)propane)] [23] $[\text{Pt}(\text{SeC}_5\text{H}_4\text{N})_2((\text{P}\cap\text{P}))]$ ($\text{P}\cap\text{P} = \text{dppm}, \text{dppp}$) [24] and the ligands $(\text{SeC}_5\text{H}_4\text{N})_2$, [25] were prepared by literature methods. The metal precursors MCl_2 ($\text{M} = \text{Zn}, \text{Cd}$); $[\text{M}(\text{OAc})_2] \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Zn}, \text{Cd}, \text{Hg}, \text{Cu}$) were procured from stern chemical. All reactions were carried out under a nitrogen atmosphere in dry and distilled analytical grade solvents at room temperature. The ^1H , $^{31}\text{P}\{^1\text{H}\}$, $^{77}\text{Se}\{^1\text{H}\}$ and $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker Avance-II spectrometer operating at 300, 121.49, 57.23 and 64.52 MHz, respectively. Chemical shifts are relative to internal chloroform (δ 7.26) for ^1H , external 85% H_3PO_4 for ^{31}P , and external Me_2Se for $^{77}\text{Se}\{^1\text{H}\}$ and Na_2PtCl_6 in D_2O for ^{195}Pt NMR. Elemental analyses were carried out on a Thermo Fischer Flash EA1112 CHNS analyzer.

Intensity data for $[\{\text{Pt}(\text{C}_5\text{H}_4\text{N})(\text{SeC}_5\text{H}_4\text{N})(\text{dppp})\}\text{ZnCl}_2]$ was measured on Bruker Apex-II, CCD diffractometer with $\text{MoK}\alpha$ radiation, and Mercury CCD were used. The structures were solved by direct methods or charge flipping [26] and refinement [27] was on F^2 using data that had been corrected for absorption effects with an empirical procedure. Non-hydrogen atoms were modeled with anisotropic displacement parameters, hydrogen atoms in their calculated

positions. Molecular structures were drawn using ORTEP [28]. Crystallographic and structural determination data are listed in Table 1.

2.2 *Synthesis of complexes*

2.2.1. *[Pt(SeC₅H₄N)₂(dppm)] (1)*

To a dichloromethane suspension (10 cm³) of [PtCl₂(dppm)] (531 mg, 0.81 mmole) was added a methanol-benzene solution (15 cm³) of NaSeC₅H₄N [prepared from (SeC₅H₄N)₂ (255 mg, 0.81 mmol) in benzene and NaBH₄ (70 mg, 1.89 mmol) in methanol]. The mixture was stirred for 6 h, after which a clear yellow solution was obtained. The latter was dried under reduced pressure and thoroughly washed with diethyl ether followed by hexane. The residue was extracted with dichloromethane through Florisil. Yellow crystalline powder was obtained. (Yield 569 mg, 78%). Anal. calcd. for C₃₅H₃₀N₂P₂PtSe₂: C, 47.04; H, 3.38, N; 3.13%. Found: C, 46.93; H, 3.34; N; 3.09%. ³¹P{¹H} NMR (CDCl₃) δ: -50.41 [(¹J (Pt-P) = 2704 Hz)]. The characterization data are consistent with literature value [24].

2.2.2. *[PtCl₂(dppm)] (1a)*

(i) To a benzene solution (10 cm³) of [Pt(SeC₅H₄N)₂(dppm)] (150 mg, 0.17 mmol), a methanolic solution (30 cm³) of Zn(OAc)₂·2H₂O (38 mg, 0.17 mmol) was added with stirring which continued for 4 h at room temperature. The solvent was evaporated under vacuum and the residue was extracted with dichloromethane and passed through cellite. The extractant on slow evaporation afforded pale white powder of [PtCl₂(dppm)] (yield 52 mg, 48% m.p. 330°C (dec.)). Anal. calcd. for C₂₅H₂₂Cl₂P₂Pt: C, 46.17; H, 3.41%. Found: C, 45.98; H, 3.36%. ¹H NMR (CDCl₃) δ: 4.35 (br, P-CH₂), 7.32-7.68 (m, Ph); ³¹P{¹H} NMR (CDCl₃) δ: -64.2 [¹J(Pt-P) = 3081

Hz]. Similarly the reaction between $[\text{Pt}(\text{SeC}_5\text{H}_4\text{N})_2(\text{dppm})]$ (100 mg, 0.11 mmol) and ZnCl_2 (17 mg, 0.12 mmol) in dichloromethane solution afforded white powder of **1** (yield 40 mg, 55%). Anal. calcd. for $\text{C}_{25}\text{H}_{22}\text{Cl}_2\text{P}_2\text{Pt}$: C, 46.17; H, 3.41%. Found: C, 46.14; H, 3.46%. ^1H NMR (CDCl_3) δ : 3.93 (m, P- CH_2), 7.54–7.71 (m, Ph); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ : -64.4 [$^1\text{J}(\text{Pt-P}) = 3087$ Hz].

(ii) Prepared similar to **1a** (method i) by using $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (46 mg, 0.17 mmol) and $[\text{Pt}(\text{SeC}_5\text{H}_4\text{N})_2(\text{dppm})]$ (150 mg, 0.17 mmol), after processing and recrystallization in dichloromethane and hexane mixture, white powder of compound **1a** (yield 60 mg, 55%) was obtained. ^1H NMR (CDCl_3) δ : 4.31 (m, P- CH_2), 7.43–7.67 (m, Ph); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ : -64.4 [$^1\text{J}(\text{Pt-P}) = 3087$ Hz]. Even the reaction between $[\text{Pt}(\text{SeC}_5\text{H}_4\text{N})_2(\text{dppm})]$ (85 mg, 0.10 mmol) and CdCl_2 (19 mg, 0.10 mmol) also resulted the product **1a** (yield 40 mg, 65%) as mentioned above. The ^1H NMR and $^{31}\text{P}\{^1\text{H}\}$ spectra were consistent with the sample prepared as in (i).

(iii) Similarly to method (i) product **1a** obtained by the reaction between $\text{Hg}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (60 mg, 0.17 mmol) and $[\text{Pt}(\text{SeC}_5\text{H}_4\text{N})_2(\text{dppm})]$ (46 mg, 0.17 mmol) on recrystallization in dichloromethane-hexane mixture. NMR spectra (^1H and ^{31}P) were consistent with compound **1a** (yield 64 mg, 59%).

2.2.3. $[\text{Pt}(\text{SeC}_5\text{H}_4\text{N})_2(\text{dppp})]$ (2)

Prepared similar way to **1** by using the $[\text{PtCl}_2(\text{dppp})]$ (485 mg, 0.71 mmole) and $\text{NaSeC}_5\text{H}_4\text{N}$ [prepared from $(\text{SeC}_5\text{H}_4\text{N})_2$ (224 mg, 0.71 mmol) in benzene and NaBH_4 (56 mg,

1.45 mmol) in methanol] and recrystallized with dichloromethane-hexane to give a yellow powder (yield 533 mg, 81%). Anal. calcd. for $C_{37}H_{34}N_2P_2PtSe_2$: C, 48.22; H, 3.72, N; 3.04%. Found: C, 48.25; H, 3.76; N; 3.04%. 1H NMR ($CDCl_3$) δ : 2.83 (br); 3.14–3.23 (m, CH_2); 6.61–7.83 (m, Ph + C_5H_4N) 8.13 (d, 4.8 Hz, 2-H, C_5H_4N). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ : -10.1 [$(^1J(Pt-P) = 2760$ Hz)].

2.2.4. [$\{Pt(C_5H_4N)(SeC_5H_4N)(dppp)\}ZnCl_2$] (2a)

To a benzene solution (12 cm^3) of $[Pt(SeC_5H_4N)_2(dppp)]$ (90 mg, 0.10 mmol) was added a methanol- solution (10 cm^3) of $Zn(OAc)_2 \cdot 2H_2O$ (22 mg, 0.10 mmol). The reactants were stirred for 5 h at room temperature to give a yellow solution. The solvents were removed under vacuum and the residue was washed with diethyl ether and dried under reduced pressure. The product was extracted with dichloromethane, filtered and passed through a Florisil column. The resulting solution was concentrated (5 cm^3) under vacuum which on refrigeration at $-4^\circ C$ gave pale yellow crystals (yield 49 mg, 52%). Anal. calcd. for $C_{37}H_{34}Cl_2N_2P_2PtSe_2Zn$: C, 45.39; H, 3.50, N; 2.86%. Found: C, 45.85; H, 3.46; N; 2.69%. 1H NMR ($CDCl_3$) δ : 2.84 (br, $-PCH_2$), 3.1 (br, PCH_2-CH_2-), 6.80 (br, C_5H_4N) 7.32 (br, Ph), 7.61 (br, Ph), 7.78-7.80 (m, Ph + C_5H_4N), 8.26 (6.2 Hz, 2-H, C_5H_4N); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ : -8.06 [$(^1J Pt-P) = 2846$ Hz)], -10.34 (satellites were merged with the former one so it is difficult to resolve.) $^{77}Se\{^1H\}$ NMR ($CDCl_3$) δ : 156.1 [$(^1J(Pt-Se) = 614$ Hz)].

2.2.5. [$\{Pt(SeC_5H_4N)_2(dppp)\}CdCl(OAc)$] (2b)

To a benzene solution (15 cm^3) of $[Pt(SeC_5H_4N)_2(dppp)]$ (150 mg, 0.16 mmol) was added a methanol- solution (15 cm^3) of $Cd(OAc)_2 \cdot 2H_2O$ (44 mg, 0.16 mmol). The reactants were

stirred for 5 h at room temperature to give a turbid yellow solution. The resulting solution is passed through G-3 assembly, clear yellow solution was collected. The solvents were removed under vacuum and the residue was washed with diethyl ether and dried under reduced pressure. The product was extracted with dichloromethane, filtered and passed through a Florisil column. The resulting solution was concentrated (3 cm³) under vacuum which on slow evaporation at room temperature gave yellow crystals (yield 101 mg, 55%). Anal. calcd. for C₃₉H₃₇ClN₂O₂P₂CdPtSe₂: C, 41.51; H, 3.30, N; 2.48%. Found: C, 42.01; H, 3.32; N; 2.49%. ¹H NMR (CDCl₃) δ: 2.11(s, -PCH₂), 2.94 (br, -PCH₂CH₂), 3.73(s, CH₃), 6.92 (d, 6.3 Hz, C₅H₄N) 7.44 (br, Ph), 7.62 (br, Ph), 7.75-7.81 (m, Ph + C₅H₄N), 8.48 (d, 4.5 Hz, 2-H, C₅H₄N); ³¹P{¹H} NMR (CDCl₃) δ: -7.53 [¹J(Pt-P) = 2880 Hz], -11.29 [¹J(Pt-P) = 3139 Hz]; ⁷⁷Se{¹H} NMR (CDCl₃) δ: 83.0 [¹J(Pt-Se) = 832 Hz], 196.7 [¹J(Pt-Se) = 660 Hz].

2.2.6. [*Pt(SeC₅H₄N)₂(dppp)*]*HgCl(OAc)* (*2c*)

Prepared in a similar fashion to **2b** by using [Pt(SeC₅H₄N)₂(dppp)] (140 mg, 0.15 mmol) and Hg(OAc)₂·2H₂O (48 mg, 0.15 mmol) and recrystallized from dichloromethane as yellow powder in yield 49% (91 mg). Anal. calcd. for C₃₉H₃₇ClN₂O₂P₂HgPtSe₂: C, 38.49; H, 3.06, N; 2.30%. Found: C, 38.91; H, 3.08; N; 2.62%. ¹H NMR (CDCl₃) δ: 2.83(s, -PCH₂), 2.99 (br, -PCH₂CH₂), 3.72 (s, CH₃), 6.92 (br, C₅H₄N), 7.35-7.45 (m, Ph + C₅H₄N), 7.66-7.72 (m, Ph + C₅H₄N), 8.12 (d, 5.4 Hz, 2-H, C₅H₄N); ³¹P{¹H} NMR (CDCl₃) δ: -7.43 [¹J(Pt-P) = 2876 Hz], -11.58 [¹J(Pt-P) = 3195 Hz]. On keeping the compound for crystallization in CH₂Cl₂ results decomposition of product with settlement of black pasty mass.

2.2.7. $[\{Pt(SeC_5H_4N)_2(dppp)\}Cu(OAc)_2]$ (**2d**)

Prepared similar way to **2b** by using $[Pt(SeC_5H_4N)_2(dppp)]$ (125 mg, 0.14 mmol) and $Cu(OAc)_2 \cdot 2H_2O$ (27 mg, 0.14 mmol) in yield 61% (91 mg). Anal. calcd. for $C_{41}H_{40}N_2O_4P_2CuPtSe_2$: C, 44.63; H, 3.65, N; 2.54%. Found: C, 44.69; H, 3.68; N; 2.56%. 1H NMR ($CDCl_3$) δ : phosphine protons could not be resolved, 3.56(s, CH_3), 6.95-7.03 (m, Ph + C_5H_4N), 7.45 (br, Ph), 7.59 (br, Ph), 7.62-7.94 (m, Ph + C_5H_4N), 8.19 (d, 6.4 Hz, 2-H, C_5H_4N); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ : - 7.53 [$^1J(Pt-P) = 2848$ Hz], -11.41 [$^1J(Pt-P) = 3158$ Hz], 32.65 (phosphine oxide); $^{77}Se\{^1H\}$ NMR ($CDCl_3$) δ : 102.3 [$^1J(Pt-Se) = 850$ Hz], 140.5 [$^1J(Pt-Se) = 620$ Hz]; $^{195}Pt\{^1H\}$ NMR ($CDCl_3$) δ : - 4411, - 4455 (dd, [$^1J(Pt-P) = 2869$ Hz], [$^1J(Pt-P) = 3158$ Hz])). One more resonance appears on longer acquisition. $^{195}Pt\{^1H\}$ NMR: - 4700 (t, [$^1J(Pt-P) = 2718$ Hz]) (presumably belongs to $[\{Pt(SeC_5H_4N)_2(dppp)\}Cu(OAc)_2]$).

3. Results and Discussion

When one mole of $[PtCl_2(P\cap P)]$ ($P\cap P = dppm, dppp$) was treated with two equivalents of $NaSeC_5H_4N$, (prepared by reductive cleavage of the Se-Se bond in di-2-pyridyl diselenide with $NaBH_4$), afforded mononuclear pyridylselenolate complexes of type $[Pt(SeC_5H_4N)_2(P\cap P)]$ ($P\cap P = dppm, dppp$). The $^{31}P\{^1H\}$ NMR spectrum exhibited single resonance at ~ -50.4 and -10.1 ppm with $^{195}Pt-^{31}P$ coupling of 2704 and 2755 Hz for dppm, dppp analogue respectively. The negative value of chemical shift considered as chelating behaviour of phosphine. The magnitude of $^1J(Pt-P)$ for compound **1** and **2** showed presence of selenolate group *trans* to the phosphine ligand [24].

The reaction of $[Pt(SeC_5H_4N)_2(dppm)]$ with one equivalent of ZnX_2 ($X = OAc, Cl$) gave an off white powder which on extraction with dichloromethane resulted a product of composition $[PtCl_2(dppm)]$. Alternatively, compound **1a** was formed when a in dichloromethane

solution of platinum precursor, $[\text{Pt}(\text{SeC}_5\text{H}_4\text{N})_2(\text{dppm})]$, was treated with MX_2 ($\text{M} = \text{Cd}, \text{Hg}; \text{X} = \text{OAc}, \text{Cl}$) in same solvent. The ^{31}P NMR spectra of **1a** displayed a single resonance at $\delta \sim -64$ ppm with $^{195}\text{Pt}-^{31}\text{P}$ coupling of ~ 2600 Hz indicative a strong trans influence of chloro group [23]. The complexes **1a** appear to be formed due to nucleophilic attack at coordinated selenolate ligand by chlorinated solvent like CDCl_3 or CH_2Cl_2 . Nucleophilic attack of chlorinated solvent at coordinated selenolate ligand is well known [29].

However, reactions of $[\text{Pt}(\text{SeC}_5\text{H}_4\text{N})_2(\text{dppp})]$ with $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ at room temperature yielded pale yellow product of $[\{\text{Pt}(\text{C}_5\text{H}_4\text{N})(\text{SeC}_5\text{H}_4\text{N})(\text{dppp})\}\text{ZnCl}_2]$ (**2a**). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **2a** displayed two resonances at -8.06 and -10.34 ppm which were flanked by their ^{195}Pt satellites. The magnitude of $^1\text{J}(\text{Pt}-\text{P})$ indicates that the phosphine ligand is *trans* to selenolate ligand [30]. However coupling *trans* to carbon centre was not resolvable. The $^{77}\text{Se}\{^1\text{H}\}$ NMR spectrum of $[\{\text{Pt}(\text{C}_5\text{H}_4\text{N})(\text{SeC}_5\text{H}_4\text{N})(\text{dppp})\}\text{ZnCl}_2]$ (**2a**) displayed a triplet at 156 ppm with platinum satellites ($^1\text{J}(\text{Pt}-\text{Se}) = 614$ Hz). The observed triplet in fact is due to coupling with platinum nuclei. In the complex **2a**, the unexpected loss of chalcogen atom is well documented in literature [14, 30-32]. For instance, reaction of Zinc metal precursor with $[\text{Pt}_2(\text{P}-\text{P})_2(\mu-\text{S})_2]$ ($\text{P}-\text{P} = \text{PPh}_3, \text{PMe}_2\text{Ph}, \text{dppp}, \text{dppy}$) did not afford the expected product, instead product $[\text{Pt}_2\text{Cl}(\text{P}-\text{P})_2(\mu-\text{S}_2\text{CH}_2)]\text{PF}_6$ ($\text{P}-\text{P} = \text{PPh}_3, \text{PMe}_2\text{Ph}, \text{dppp}, \text{dppy}$) formed by the decomposition of $[(\text{P}-\text{P})_2\text{Pt}_2(\mu_3-\text{S})_2\text{Zn}][\text{PF}_6]_2$ in CH_2Cl_2 [30, 32]. Similarly, the bridging thio complex $[\text{Pt}_2(\text{dppf})_2(\mu-\text{S})_2]$ in dichloromethane solution yields mononuclear compound $[\text{Pt}(\text{SCH}_2\text{Cl})_2(\text{dppf})]$ which indicates the formation of terminal bis thiolato complexes from the bridging one [31]. In the present study, the removal of selenium atom and acetate group appears to be brought out by strong nucleophilicity of CH_2Cl_2 .

Similarly, an addition product [$\text{Pt}(\text{SeC}_5\text{H}_4\text{N})_2(\text{dppp})\text{MX}_2$] ($\text{M} = \text{Cd}, \text{Hg}, \text{Cu}$; $\text{X} = \text{OAc}, \text{Cl}$) could also be obtained by the reaction of [$\text{Pt}(\text{SeC}_5\text{H}_4\text{N})_2(\text{dppp})$] with $\text{MOAc}_2 \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Cd}, \text{Hg}, \text{Cu}$). Unlike the [$\text{M}\{\text{Pt}_2(\text{P-P})_2(\mu_3\text{-S})_2\}\text{X}_2$] ($\text{M} = \text{Zn}, \text{Cd}$ and Hg , $\text{P-P} = \text{PPh}_3, \text{dppe}$) in the reported case the metal center like $\text{Zn}, \text{Cd}, \text{Hg}$ has only attached with one selenium atom which was corroborated by NMR and crystal structure of complex **2b**. The ^{31}P NMR spectrum of complex **2b, 2c, 2d** exhibited two ^{31}P resonance at $\delta \sim -7$ ppm and -11 ppm with different $^1\text{J}(\text{Pt-P})$ coupling constants. The former resonance is deshielded compared to latter one, with $^{195}\text{Pt}-^{31}\text{P}$ coupling of ~ 2850 Hz indicative of selenolate ligand *trans* to the phosphine ligand [33-35]. While latter resonance ~ -11 ppm with the coupling constant ~ 3150 Hz is phenomenal agreement with reported heterometallic complexes [$\text{M}\{\text{Pt}_2(\text{dppe})_2(\mu_3\text{-S})_2\}\text{X}_2$] ($\text{M} = \text{Zn}, \text{Cd}$ and Hg) [29, 36]. Hence, this resonance belongs to selenolate ligand which is attached to platinum as well as with $\text{Cd}, \text{Hg}, \text{Cu}$ also. Due to bonding with latter metal centres, electron density around selenium atom gets reduced. As a result it showed shielded resonance compares to other one [36]. The $^{77}\text{Se}\{^1\text{H}\}$ NMR spectrum of complex **2b** displayed two different resonance at 83 ppm and 196 ppm with their platinum satellite. Two dissimilar resonances correspond to un-equivalent type of selenium. It seems that in complex [$\text{Pt}(\text{SeC}_5\text{H}_4\text{N})_2(\text{dppp})\text{MX}_2$] ($\text{M} = \text{Cd}, \text{Hg}, \text{Cu}$), chlorinated solvent ($\text{CH}_2\text{Cl}_2, \text{CDCl}_3$) partially substituted the acetate group from metal acetate due to their strong nucleophilicity [14, 29].

The presence of two different selenolate ligand in above discussed compound is further corroborated by ^{195}Pt NMR spectrum of [$\text{Pt}(\text{SeC}_5\text{H}_4\text{N})_2(\text{dppp})\text{CuCl}(\text{OAc})$] which showed a doublet of doublet centered at -4411 ppm [$^1\text{J}(\text{Pt-P}) = 2869$ Hz], -4455 ppm [$^1\text{J}(\text{Pt-P}) = 3158$ Hz] [37-38]. Apparently, during the longer acquisition ^{195}Pt NMR spectrum of **2d** also displayed a triplet at $\delta = -4700$ ppm [$^1\text{J}(\text{Pt-P}) = 2718$ Hz] as well, indicating coordination of two

equivalent phosphorus nuclei [39]. The appearance of new resonance suggests the slowly disintegration of compound in CDCl_3 solution to give an unknown moiety. This decomposition is probably facilitated by nucleophilic attack of chlorinated solvent [29].

Crystal structures

Molecular structures of $[\{\text{Pt}(\text{C}_5\text{H}_4\text{N})(\text{SeC}_5\text{H}_4\text{N})(\text{dppp})\}\text{ZnCl}_2]$ was established by single crystal X-ray diffraction analyses. ORTEP drawings with atomic numbering scheme are depicted in Figures 1 while selected inter-atomic parameters are given in Tables 2.

The platinum atom in the complex $[\{\text{Pt}(\text{C}_5\text{H}_4\text{N})(\text{SeC}_5\text{H}_4\text{N})(\text{dppp})\}\text{ZnCl}_2]$ (**2a**) adopts a distorted square planar geometry defined by *trans* “ P_2SeC ” coordination environment while the zinc atom acquires distorted tetrahedral shape. The Pt...Zn (3.1526(13) Å) bond is in close proximity but not lie in metal - metal bonding range [36]. The Pt–Se (2.4821(11) Å), distance is slightly longer than the normal metal chalcogen reported for the known heterometallic complex, $[\text{Zn}\{\text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4\}\text{Cl}_2]$ (2.352(2) / 2.378(2) Å) [29], $[\text{Zn}\{\text{Pt}_2(\mu\text{-S})_2(\text{dppe})_4\}\text{Cl}_2]$ (2.374(7) – 2.379(7) Å) [36] however in good conformity with those reported for $[\{\text{Pt}_2(\text{dppy})_4(\mu_3\text{-Se})_2\}_2\text{Ag}_3](\text{PF}_6)_3$ (2.459(1) – 2.477(1) Å) [15]; $\{\text{Pt}_2(\mu_3\text{-Se})_2(\text{PPh}_3)_4[\text{Pt}(\text{cod})]\}\{\text{PF}_6\}_2$ (2.4392(6) – 2.4919(6) Å) [40]. The Pt–C (2.015(10) Å) distance is in agreement with the one reported for $[\text{PtX}(\text{Ph})(\text{PPh}_3)_2]$ (X = Cl, I) (Pt–C = 2.01(1), 2.015(9) Å) [35, 36]. The Zn–N and Zn–Cl distances are as expected [29, 36, 43-46].

The molecular structure of complex $[\{\text{Pt}(\text{SeC}_5\text{H}_4\text{N})_2(\text{dppp})\}\text{CdCl}(\text{OAc})]$ (**2b**) is solvated in nature. The complex shows eight member puckered ring restrained between platinum and cadmium metal center. The geometry around the Pt metal center is confined with ‘ P_2Se_2 ’ fragments with distorted square planar geometry however Cd atom opts distorted octahedral shape which is defined with ‘ $\text{N}_2\text{O}_2\text{Cl}$ ’ frame with Cl and Se atom at axial position. The Pt–P and

Pt–Se distances are as expected [29, 36]. Due to a poor refinement of the complex, structural data is not reported here. The Cd–N distances ($2.36_{\text{avg}} \text{ \AA}$) are well in agreement with the reported values [47-49]. The Cd...Se ($2.969(4) \text{ \AA}$) are slightly longer than the reported value for $[\text{Cd}\{\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4\}\text{Cl}_2]$ (Cd...Se = $[2.6852(10) \text{ \AA}]$) [19], $[\text{Cd}\{\text{Pt}_2(\mu\text{-S})_2(\text{dppe})_4\}\text{Cl}_2]$ (Cd...S = $2.561(2) - 2.553(2) \text{ \AA}$) [36]. Because of these interactions Cd...Se pyridyl selenolate group move out from metal plane.

4. Conclusion

The reactions of d^{10} metal precursors with platinum selenolato compounds $[\text{Pt}(\text{SeC}_5\text{H}_4\text{N})_2(\text{P}\cap\text{P})]$ ($\text{P}\cap\text{P} = \text{dppm}, \text{dppp}$) yield a different type of complexes depending on the nature of the phosphine ligand and d^{10} metal centre. In comparison to dppm analogue, the complex $[\text{Pt}(\text{SeC}_5\text{H}_4\text{N})_2(\text{dppp})]$ is nucleophilic enough to trap the metal precursor of d^{10} system results an addition product.

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Supporting Information

CCDC-Nos. 1497006 for $[\text{Pt}(\text{C}_5\text{H}_4\text{N})(\text{SeC}_5\text{H}_4\text{N})(\text{dppp})]\cdot\text{ZnCl}_2$, and contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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Table 1. Crystallographic and structural determination data for [Pt(C₅H₄N)(SeC₅H₄N)(dppp)].ZnCl₂ (**2a**)

Complex	[Pt(SeC ₅ H ₄ N)(C ₅ H ₄ N) (dppp)].ZnCl ₂
Chemical formula	C ₃₇ H ₃₄ N ₂ Cl ₂ P ₂ PtSeZn
Formula wt.	978.92
Crystal size (mm ³)	0.30 x 0.30 x 0.20
Radiation used for data collection	Mo-K _α
Crystal system	Monoclinic
Space group	P1 _{21/c}
Unit cell dimensions	
a (Å)	20.307(7)
b(Å)	8.971(3)
c(Å)	21.000(4)
α(°)	90
β(°)	103.02(4)
γ(°)	90
Volume (Å ³)	3727(2)
Z	4
ρ _{calcd} , g cm ⁻³	1.744
θ for data collection (°)	7.8-10.9
μ (mm ⁻¹)/F(000)	5.627 / 1904
Index range	-25 ≤ h ≤ 26 -11 ≤ k ≤ 0 -27 ≤ l ≤ 15
No of reflections collected	10213
No of independent reflection / No. of observed reflections with I > 2σI	9922 / 4457
Data/restraints/parameters	9922 / 0 / 484
Final R ₁ , ωR ₂ indices	0.0474 / 0.0905
R ₁ , ωR ₂ (all data)	0.1702 / 0.1211
Goodness of fit on F ²	0.932

Table 2. Selected bond lengths (Å) and angles (°) of [Pt(SeC₅H₄N)(C₅H₄N) (dppp)].ZnCl₂ (**2a**)

Pt1–P1	2.279(3)	Pt1–P2	2.335(3)
Pt1–Se1	2.4821(11)	Pt1–C1	2.015(10)
Zn1–N1	2.013(8)	Zn–N2	2.084(9)
Zn1–Cl1	2.255(3)	Zn1–Cl2	2.282(3)
Pt1–Zn1	3.1526(13)	Se1–C6	1.903(11)
P1–Pt1–P2	94.24(9)	C1–Pt1–Se1	85.4(3)
P1–Pt1–C1	88.0(3)	P2–Pt1–Se1	92.37(8)
P1–Pt1–Se1	172.09(7)	P2–Pt1–C1	177.8(3)
C6–Se1–Pt1	108.1(4)	N1–C1–Pt1	116.5(7))
Se1–Pt1–Zn1	82.55(4)	C1–Pt1–Zn1	63.3(3)
P1–Pt1–Zn1	98.34(7)	P2–Pt1–Zn1	116.42(8)
N1–Zn1–Cl1	125.4(2)	N2–Zn1–Cl2	103.1(3)
N1–Zn1–Cl2	102.1(2)	N2–Zn1–Cl1	105.6(3)
Cl1–Zn1–Cl2	107.72(11)	N1–Zn1–N2	110.8(4)
N1–Zn1–Pt1	63.5(2)	N2–Zn1–Pt1	86.6(3)
Cl1–Zn1–Pt1	79.91(8)	Cl2–Zn–Pt2	165.07(9)

Figure Captions

Figure 1. ORTEP drawing of $[\text{Pt}(\text{C}_5\text{H}_4\text{N})(\text{SeC}_5\text{H}_4\text{N})(\text{dppp})]\cdot\text{ZnCl}_2$ with atomic number scheme.

Hydrogen atoms are omitted for clarity. The ellipsoids were drawn at the 50% probability.

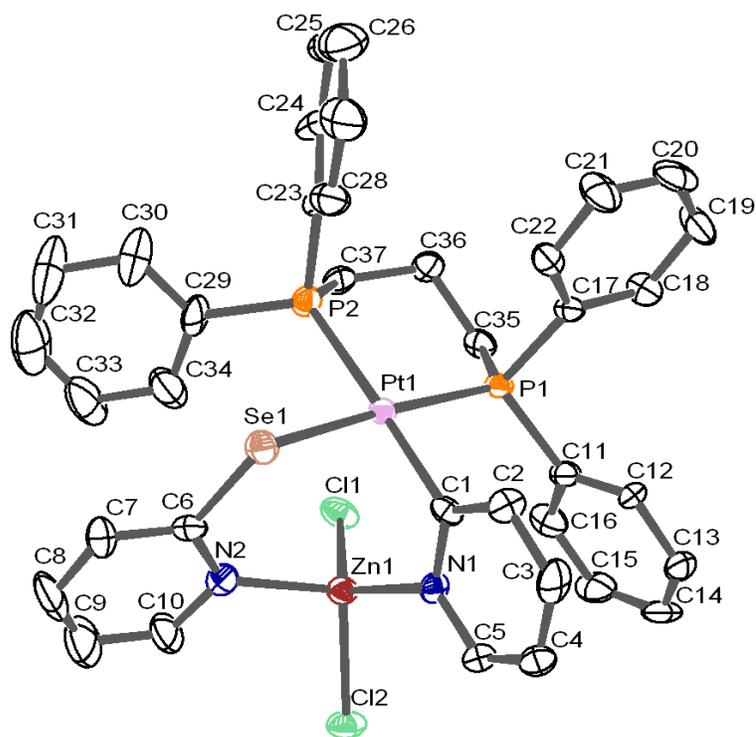
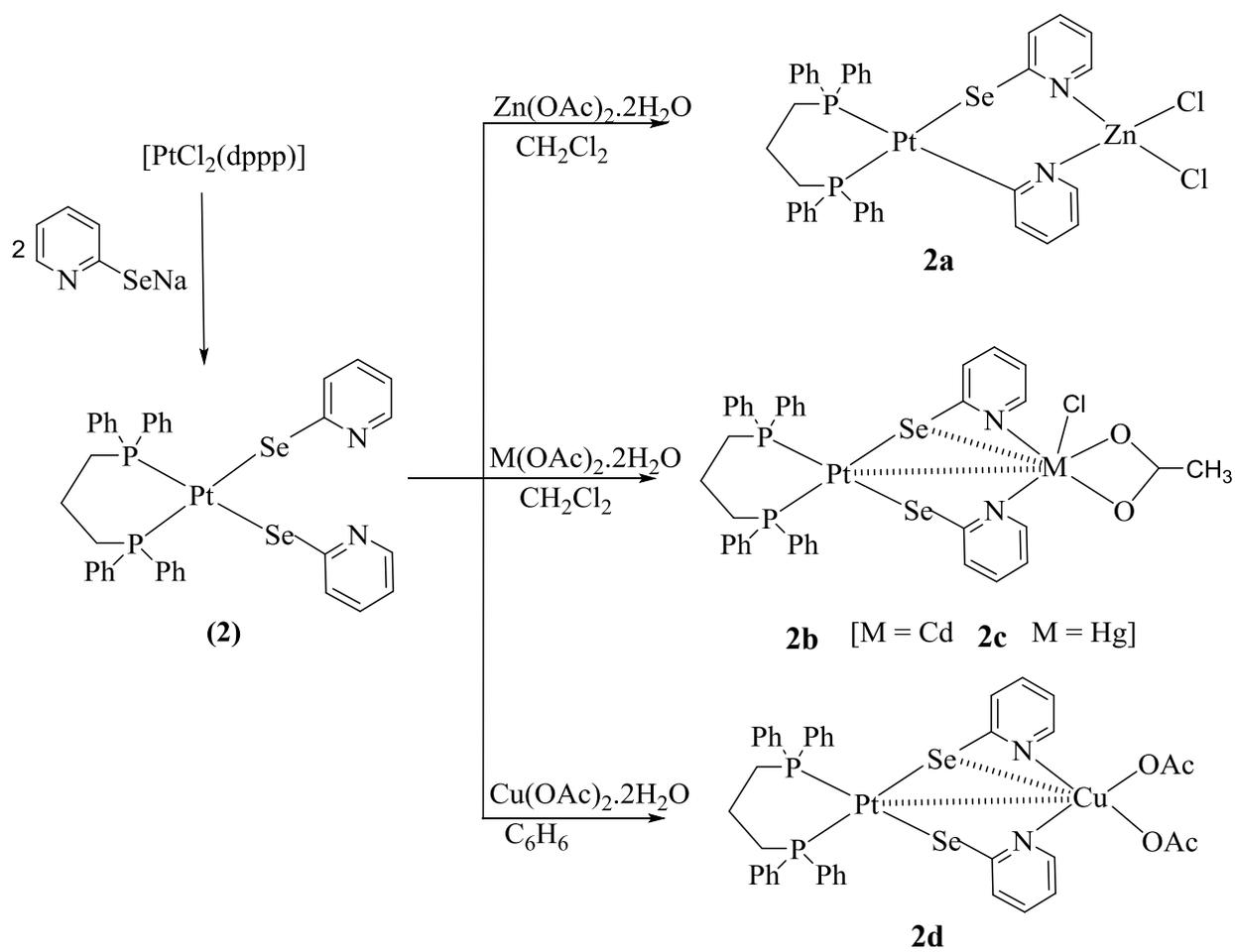


Figure 1. ORTEP drawing of $[\text{Pt}(\text{C}_5\text{H}_4\text{N})(\text{SeC}_5\text{H}_4\text{N})(\text{dppp})].\text{ZnCl}_2$ (**1**) with atomic number scheme. The ellipsoids were drawn at the 50% probability.



Scheme 1