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# Dinuclear Pd<sup>II</sup>/Pt<sup>II</sup> complexes [M<sub>2</sub>(phosphine)<sub>n</sub>(thio-ligand)<sub>3</sub>]Cl incorporating N, S-bridged pyridine-2-thiolate and benzimidazoline-2-thiolate

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#### ABSTRACT

Equimolar reaction of [PdCl<sub>2</sub>(dppm)] {dppm = bis(diphenylphosphino) methane} with pyridine-2-thione (pySH) in presence of NaOH base in aqueous ethanol formed dinuclear mixed- ligand complex, [Pd<sup>II</sup><sub>2</sub>( $\mu$ - $\kappa^2$  :N,S-pyS)<sub>3</sub>( $\mu$ -P,P-dppm)]Cl **1**. Similarly, reaction of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> with benzimidazoline-2-thione (bzimSH) in 1 : 2 molar ratio in the presence of Et<sub>3</sub>N base in acetonitrile has formed a dinuclear complex, [Pd<sup>II</sup><sub>2</sub>( $\mu$ - $\kappa^2$ :N,S-bzimS)<sub>2</sub>( $\kappa^1$ -S-bzimS)(PPh<sub>3</sub>)<sub>3</sub>]Cl· 2H<sub>2</sub>O **2.** Surprisingly, analogous thio-ligand, 1,3-imidazoline-2-thione (imzSH), merely formed a simple square planar complex, [Pd( $\kappa^1$ -S-imzSH)<sub>4</sub>]Cl<sub>2</sub>·2H<sub>2</sub>O **3**. The reaction of H<sub>2</sub>PtCl<sub>6</sub> with pySH and dppm (1:1:1 molar ratio) in the presence of Et<sub>3</sub>N base in toluene –ethanol (1 :1 :: v/v) mixture also formed a mixed-ligand dinuclear complex [Pt<sup>II</sup><sub>2</sub>( $\mu$ - $\kappa^2$  :N,S-pyS)<sub>3</sub>( $\mu$ -P,P-dppm)]Cl similar to **1**. All these complexes have been characterized using analytical data, IR, NMR (<sup>1</sup>H, <sup>31</sup>P), UV-visible, fluorescence, ESI-mass and single crystal x-ray crystallographic techniques. The anionic thio-ligands are N,S-bridged in complexes **1** and **4**, both N,S-bridged and  $\kappa^1$ -S bonded in **2** and as neutral  $\kappa^1$ -S bonded in **3**. There are short M····M contacts in **1** and **4** (**1**: 2.7249(5) Å; **4**: 2.7350(8) Å). Complexes **1**, **3** and **4** showed intense fluorescence. ESI mass spectral studies of **1**, **3** and **4** revealed the formation of molecular ions and other species.

*Keywords:* Pyridine-2-thione, 1, 3-benzimidazoline-2-thione, 1, 3- imidazoline-2-thione, palladium(II) chloride, platinum.

#### 1. Introduction

Heterocyclic thioamides incorporating N, S donor atoms constitute an important class of thioligands whose coordination chemistry has been in focus of several research workers [1-29]. These thio ligands have shown interesting coordination variability which has resulted in the formation of a diverse range of coordination compounds: mononuclear, dinuclear, oligomers and polymers [10-12, 14, 18, 22-24, 27]. Another interest in the chemistry of heterocyclic thioamides is linked to their biological applications such as anticancer [30-34], antimicrobial/ antibacterial [35, 36] and catalysis [37, 38].



Chart 1. Molecular structures of thio-ligands

The reactions of  $Pd^{II}/Pt^{II / III}$  with a series of heterocyclic thioamides (Chart 1) have yielded a variety of complexes with and without co-ligands. For example, without co-ligands, Pd/ Pt have formed mononuclear and dinuclear complexes of the type:  $[Pt^{II}(\kappa^1-S-pySH)_4]Cl_2$  [15],  $[Pd^{II}(\kappa^1-S-mimzSH)_4]Cl_2 \cdot 2H_2O$  [39],  $[Pt^{II}(\kappa^1-S-mimzSH)_4]Cl_2$  [40],  $[Pd^{II}_2(\mu-\kappa^2:N,S-pyS)_4]$  [41, 42] and  $[Pt^{III}_2Cl_2(\mu-\kappa^2:N,S-pyS)_4]$  [43]. The co-ligands used are mono- and di-tertiary phosphines and a brief list of  $Pd^{II}/Pt^{II}$  complexes with pyridine-2-thione (pySH), pyrimidine-2thione (pymSH) and purine-6-thione (purSH<sub>2</sub>) (Chart 1) is listed here. Two types of complexes are formed: (a) mononuclear  $[PdCl(\kappa^2:N,S-pyS)(PPh_3)]$  [44], cis- $[M(L_n)(P, P-L)]$  {M = Pd, Pt;

$$\begin{split} &L_n = 2(\kappa^1:S\text{-}pyS), \ 2(\kappa^1:S\text{-}pymS), \ \kappa^2\text{-}N,S\text{-}puS; \ P, \ P\text{-}L = Ph_2P\text{-}(CH_2)_n\text{-}PPh_2; \ n = 1, \ dppm; \ 2, \ dppe; \ 3, \ dppp; \ 4, \ dppb; \ Ph_2P\text{-}CH=CH\text{-}PPh_2, \ dppen \} \ [12, \ 14, \ 21, \ 45], \ [Pt(\kappa^1:S\text{-}pyS)_2(PPh_3)_2] \ [13], \ [M(\kappa^1:S\text{-}pymS)_2(PPh_3)_2] \ (M = Pd, \ Pt) \ [45], \ [Pd(\kappa^2:N,S\text{-}pymS)(PPh_3)_2](CIO_4) \ [46], \ [Pt(\kappa^2:N,S\text{-}pyS)(PPh_3)_2](PF_6) \ [47], \ and \ (b) \ dinuclear, \ [Pd_2(\mu - \kappa^2:N,S\text{-}pyS)(\mu - \kappa^2:S\text{-}pyS)(\kappa^1:S\text{-}pyS)_2(\mu - P,P\text{-}dppm)] \ [14], \ [Pd_2(\mu - \kappa^2:N,S\text{-}pyS)_3(\kappa^2:P,P\text{-}dppm)]C1 \ [14] \ and \ [M_2Cl_2(\mu - \kappa^2:N,S\text{-}L)_2(PMe_3)_2] \ (M = Pd; \ L = pyS, \ pymS) \ [48, 49]. \end{split}$$

From this laboratory, reactions of  $[M(diphosphine)Cl_2]$  (M = Pd, Pt; diphosphine = Ph<sub>2</sub>P-CH<sub>2</sub>-CH<sub>2</sub>-PPh<sub>2</sub>, dppe; Ph<sub>2</sub>P-CH=CH-PPh<sub>2</sub>, dppen) with pyridine-2-thione in 1 : 2 molar ratio gave P, P- chelated square planar complexes, cis-M( $\kappa^2$ -P,P)( $\kappa^1$ -S-L)<sub>2</sub> (A) (Chart 2) [12]. As a curiosity, it was desired to prepare Pd/Pt complexes similar to 'A' type by reacting M(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> with 1, 3-benzimidazoline-2-thione (bzimSH) and 1, 3- imidazoline-2-thione (imzSH). The second curiosity was to react a metal salt (MCl<sub>2</sub>) with pySH and dppm in 1 : 1 : 1 molar ratio so as to obtain mixed-ligand complexes of type,  $[M_2(pyS)_2(dppm)_2]Cl_2$  (B, M = Pd/Pt). The results of these reactions are reported in this paper.



#### 2. Experimental

#### 2.1 Material and Techniques

Pyridine-2-thione, benzimidazoline-2-thione, 1,3-imidazoline-2-thione, 1,1-bis(diphenylphos - phino)methane(dppm), PPh<sub>3</sub>, PdCl<sub>2</sub> and H<sub>2</sub>PtCl<sub>6</sub> were procured from Sigma–Aldrich Ltd. The precursors, namely, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and PdCl<sub>2</sub>(dppm) were prepared by the addition of a respective phosphines to a solution of PdCl<sub>2</sub> in acetonitrile followed by refluxing for 5-6 h [50]. The melting points were determined with a Gallenkamp electrically heated apparatus. The IR spectra were recorded using KBr pellets on Varian 660 FT IR Spectrometer in the 4000-200 cm<sup>-1</sup> range.

The <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub>/ dmso-d<sub>6</sub> using a Bruker Avance II 400 NMR and Bruker Avance 500 NMR spectrometer at 400 MHz and 500 MHz respectively using TMS as an internal reference. The <sup>31</sup>P NMR spectra were recorded in CDCl<sub>3</sub> with Bruker Avance II 400 NMR at 161.97 MHz spectrometer with o-phosphoric acid as the external reference.

#### 2.2. Synthesis of complexes

#### 2.2.1. Synthesis of , $[Pd^{II}_{2}(\mu-\kappa^{2}:N,S-pyS)_{3}(\mu-P,P-dppm)]Cl$ (1)

To the solid thio-ligand pySH (0.01g, 0.090 mmol) placed in round bottom flask was added a solution of sodium hydroxide (NaOH) (0.004g, 0.09 mmol) in distilled water (2 mL) which formed a clear light yellow solution. To this solution was added a suspension of PdCl<sub>2</sub>(dppm) (0.05g, 0.089 mmol) in ethanol (15 mL) and the contents were refluxed for 10 h. The colour of the reaction mixture became dark orange and was filtered. The filtrate was evaporated using rotary evaporator until a solid was obtained. It was treated with acetone (10 mL) which dissolved the complex leaving behind NaCl. The acetone solution was filtered to remove NaCl. To the acetone extract was added 4 mL of dichloromethane-methanol (1 : 1 v/v) mixture and left to evaporate at room temperature. The orange colored crystals of compound 1 were formed in a period of 20-25 days (65 %; m.p 178-180 °C). Anal. Calc. for C<sub>40</sub>H<sub>34</sub>ClN<sub>3</sub>P<sub>2</sub>Pd<sub>2</sub>S<sub>3</sub> (963.07) : C, 49.84; H, 3.53; N, 4.36. Found: C, 49.78; H, 3.92; N, 4.48 %. IR bands(KBr, cm<sup>-1</sup>): v(C-H) 3049 m, 2924 m, 2862 m;  $v(C-C) + v(C-N) + \delta(C-H)$ , 1591 s, 1437 s, 1268 w, 1189 s; v(C-S), 1108s;  $v(P-C_{Ph})$ , 1040 w; 741 s, v(Pd-N), 504 s. <sup>1</sup>H NMR data (CDCl<sub>3</sub>,  $\delta$ , ppm, J, Hz): 9.42 (d, 1H, J = 10 Hz,  $H^6$ , pyS), 8.69 (d, 1H, J = 5 Hz,  $H^6$ , pyS), 8.50 (m, 2H,  $H^3$ , pyS), 8.24 (d, J, 5 Hz, 1H,  $H^6$ , pyS), 8.15 (m, 2H, H<sup>3</sup>, H<sup>4</sup>, pyS), 7.69 (m, 8H, o-H, Ph), 7.37 (m, 4H, p-H, Ph), 7.13 (m, 2H, H<sup>4</sup>, pvS), 6.96 (m, 9H, H<sup>5</sup>, pvS, m-H, Ph), 6.63 (m, 2H, H<sup>5</sup>, pvS), 4.41 (m, 1H, -CH<sub>2</sub>-, dppm), 4.24 (m, 1H, -CH<sub>2</sub>-, dppm). <sup>31</sup>P NMR data (CDCl<sub>3</sub>,  $\delta$  ppm):  $\delta_P = 32.46$  ppm,  $J_{P-P}$ , 61.5 Hz;  $\delta_P = 28.02$ ppm,  $J_{P-P}$ , 60 Hz. UV-vis. data, DMSO,  $\lambda_{max}$  /nm,  $\epsilon$  /Lmol<sup>-1</sup>cm<sup>-1</sup>: [10<sup>-4</sup> M] 422 (3.57 x 10<sup>3</sup>), 311  $(1.92 \times 10^4)$ , 273 (5.00 x 10<sup>4</sup>). Fluorescence data, DMSO :  $[10^{-5} \text{ M}]$  ( $\lambda_{max}^{em} = 442 \text{ nm}$ ,  $\lambda_{max}^{ex} =$ 322 nm).

#### 2.2.2. Synthesis of $[Pd^{II}_{2}(\mu-\kappa^{2}:N,S-bzimS)_{2}(\kappa^{1}-S-bzimS)(PPh_{3})_{3}]Cl\cdot 2H_{2}O$ (2)

To the solution of  $PdCl_2(PPh_3)_2$  (0.050 g, 0.07 mmol) dissolved in 10 mL of CH<sub>3</sub>CN, bzimSH (0.021 g, 0.14 mmol) was added followed by Et<sub>3</sub>N base (0.5 mL). The solution became turbid

and yellowish orange in color. Then the refluxing was done for 6 h. The colour of the reaction mixture became orange and was filtered. The filtrate was evaporated using rotary evaporator until a solid was obtained. It was treated with acetone which dissolved the complex leaving behind  $Et_3NH^+CI^-$ , white solid. The acetone solution was filtered to remove  $Et_3NH^+CI^-$ . To it was added 4 mL dichloromethane-methanol (1 : 1, v/v) mixture and left to evaporate at room temperature. The orange colored crystals of compound **2** were formed in a period of 10-15 days (67 %, m.p 218-220 °C). *Anal.* Calc. for  $C_{75}H_{61}ClN_6P_3Pd_2S_3 \cdot 2H_2O(1519.67)$  : C, 59.22; H, 4.01; N, 5.53. Found: C, 59.80; H, 4.36; N, 5.52 %. IR bands(KBr, cm<sup>-1</sup>): v(O-H), 3393 m(b); v(C-H), 3051 m, 2963 w; v(C-C) + v(C-N) +  $\delta$ (C-H), 1618 s, 1479 m, 1433 s, 1391 s, 1263 m, 1226 w; 1182 w; v(P-C\_{Ph}), 1096 s; v(C-S) 1022 s; 802 m, 741 s, 691 s, v(Pd-N), 523 s; 422 w. ESI Mass could not be recorded due to poor solubility.

#### 2.2.1. Synthesis of $[Pd(\kappa^{1}: S-imzSH)_{4}]Cl_{2}.2H_{2}O(3)$

To a suspension of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.05, 0.071 mmol) in 10 ml of CH<sub>3</sub>CN, imzSH (0.014 g, 0.14 mmol) was added in presence of Et<sub>3</sub>N base (0.5 mL). The solution became turbid orange colored and the contents were refluxed for 5-6 h. The filtrate was evaporated using rotary evaporator until a solid was obtained. The solid obtained was dissolved in methanol (10 mL) and to this was added CH<sub>3</sub>CN (2 mL) and the mixture allowed to evaporate at room temperature. The dark red crystals of compound **3** were obtained after a period of 10 days (40 %, m.p 260-262 °C). *Anal.* Calc. for C<sub>12</sub>H<sub>20</sub>Cl<sub>2</sub>N<sub>8</sub>O<sub>2</sub>PdS<sub>4</sub>(613.90): C, 23.46; H, 3.26; N, 18.24. Found: C, 23.20; H, 3.42; N, 18.40 %. IR bands(KBr, cm<sup>-1</sup>): v(O-H), 3447 m, 3384 m; v(N-H), 3308 m; v(C-H), 3081 s, 3016 w, 2968 m, 2938 m, 2847 s; v(C-C) + v(C-N) +  $\delta$ (C-H), 1581 s, 1479 s, 1401 s, 1284 w, 1232 w; v(C=S), 1119 m; 1058 m, 951 w, 910 m, 815 m, 740 s, 665 m, 497 m. <sup>1</sup>H NMR data (CDCl<sub>3</sub> + dmso-d<sub>6</sub> (8 : 2),  $\delta$ , ppm, J, Hz): 11.93 (s, NH, 1H, imzSH), 7.25 (s, 2H, C<sup>4.5</sup>H, imzSH). UV-vis. data, DMSO,  $\lambda_{max}$  /nm,  $\varepsilon$  /Lmol<sup>-1</sup>cm<sup>-1</sup>: [10<sup>-4</sup> M] ( $\lambda_{max}^{em}$  = 442 nm,  $\lambda_{max}^{ex}$  = 342 nm).

#### 2.2.1. Synthesis of $[Pt_2(\mu - \kappa^2:N, S-pyS)_3(\kappa^2:P,P-dppm)]Cl(4)$

To the solid pySH (0.013g, 0.12 mmol) suspended in toluene (5 mL) in a round bottom flask was added a solution of platinic acid,  $H_2PtCl_6$  (0.05 g, 0.12 mmol) in ethanol (15 mL) in presence of Et<sub>3</sub>N base (2 mL). The contents were stirred for 2 h until turbidity appeared and to this was

added solid dppm (0.046 g, 0.12 mmol). The clear orange color solution formed was stirred overnight and Et<sub>3</sub>NH<sup>+</sup>Cl<sup>-</sup> formed was filtered off, and the filtrate was allowed to crystallize at C40 H34 Cl N3 P2 Pt2 S3 room temperature. The orange crystals of compound **4** were formed in a period of 15-20 days (68 %, m.p 197-199 °C). *Anal.* Calc. for C<sub>40</sub>H<sub>34</sub>ClN<sub>3</sub>P<sub>2</sub>Pt<sub>2</sub>S<sub>3</sub> (1140.43): C, 42.09; H, 2.98; N, 3.68. Found: C, 42.50; H, 2.62; N, 3.56 %. IR bands(KBr, cm<sup>-1</sup>): v(O-H), 3453 s; v(C-H), 3051 w, 2926 w, 2855w; v(C-C) + v(C-N) +  $\delta$ (C-H), 1663 w, 1638 w, 1591 s, 1545 w, 1483 w, 1452 s, 1435 m, 1408 m, 1269 w, 1159 w; v(C-S), 1136 w; v(P-C<sub>Ph</sub>), 1098 m; 1053 w, 1020 w, 997 w, 739 s, 718 s, 696 s, 660 w, v(Pt-N), 530 m; 486 w, 428 w. <sup>1</sup>H NMR data (CDCl<sub>3</sub>,  $\delta$ , ppm, J, Hz): 9.13 (d, 1H, J = 5 Hz, H<sup>6</sup>, pyS), 8.43 (d, 1H, J = 10 Hz, H<sup>6</sup>, pyS), 8.36 (m, 3H, H<sup>6</sup>, H<sup>3</sup>, pyS), 8.21 (m, 2H, H<sup>3</sup>, H<sup>4</sup>, pyS), 7.70 (m, 8H, o-H, Ph), 7.42 (m, 2H, H<sup>4</sup>, pyS), 7.14 (m, 5H, p-H, Ph, H<sup>5</sup>, pyS), 6.91 (m, 8H, m-H, Ph), 6.63 (t, 1H, J, 7.5, Hz, H<sup>5</sup>, pyS), 6.56 (t, 1H, J = 7.5 Hz, H<sup>5</sup>, pyS), 4.46 (m, 1H, -CH<sub>2</sub>-, dppm), 4.33 (m, 1H, -CH<sub>2</sub>-, dppm). <sup>31</sup>P NMR data (CDCl<sub>3</sub>,  $\delta$  ppm):  $\delta_P = 12.70$  ppm,  $J_{P-P}$ , 38.87 Hz;  $\delta_P = 8.29$  ppm,  $J_{P-P}$ , 38.87 Hz. UV-vis. data, DMSO,  $\lambda_{max}$  /nm,  $\varepsilon$  /Lmol<sup>-1</sup>cm<sup>-1</sup>: [10<sup>4</sup> M] 354 (4.29 x 10<sup>3</sup>), 302 (1.29 x 10<sup>4</sup>), 273 (1.79 x 10<sup>4</sup>). Fluorescence data, DMSO : [10<sup>-5</sup> M] ( $\lambda_{max}^{em} = 439$  nm,  $\lambda_{max}^{ex} = 358$  nm).

#### 2.3 X-ray crystallography

The single crystals of compounds (1-3) were mounted on glass fibers and data were collected using Bruker CCD SMART 1000 (1), Xcalibur and Ruby, Gemini (2, 3) diffractometer, equipped with a graphite monochromator and Mo–K $\alpha$  radiation ( $\lambda = 0.71073$  Å; 1-3). The unit cell dimensions and intensity data were measured at 100(2) for 1, 173(2) for 2 and 123(2) for 3 respectively. The data were processed with Bruker SMART (data collection, cell refinement) 1, CrysAlisPro (data collection, cell refinement, data reduction) (2, 3) [51], Bruker SAINT (data reduction) (1) [52]. The structures were solved by direct methods using the program SHELXS-97 [53] (1-3) [54] and refined by full-matrix least-squares techniques against F<sup>2</sup> using SHELXL-97 [55]. The data for complex 4 were collected on Bruker APEX-II CCD at room temperature. The crystal quality was very poor and a number of crystals were tried before this data set was taken and was the best out of the lot. The structure was solved by direct methods using SIR-92[54] and it was refined by least square methods on F<sup>2</sup> using SHELXL-97 program[53]. All atoms were refined anisotropically. Hydrogen were calculated geometrically. The refinement showed a disordered Cl atom which was resolved at two positions using PART command and refining its

sof and thermal parameters as free variables. The final difference Fourier map still shows a few, small residual electron density peaks of 2.5 to 1.0 e Å<sup>3</sup> which are lying very close to heavy atoms like Pt, S and P and could not be modelled any further. These could be due to series termination error or due to underlying unresolved disorder in certain atoms but as such there is no missing atomic entity. The data quality is poor, is evident from the ratio of unique to observed reflections being only 46%. The unit cell shows large solvent accessible voids due to packing forces only. The cif shows certain B and C level alerts due to these reasons. The crystallographic data are given in (Table 1) and bond lengths and angles are placed in Table 2.

#### 3. Results and Discussion

#### 3.1 Comments on the synthesis and IR spectroscopy

When PdCl<sub>2</sub>(dppm) was reacted with pyridine-2-thione (pySH) in 1 : 2 molar ratio in aqueous NaOH in ethanol to obtain the expected complex,  $cis-Pd(\kappa^2:P,P-dppm)(\kappa^1:S-pyS)_2$ (similar to A, Chart 2) [12], no crystalline product could be isolated. On repeating this reaction in 1: 1 molar ratio under similar experimental conditions, it gave a crystalline product with unusual empirical composition, Pd<sub>2</sub>(pyS)<sub>3</sub>(dppm)·Cl. The single crystal x-ray structure determination of this product revealed the formation of a mixed-ligand dinuclear complex,  $[Pd^{II}_{2}(\mu-\kappa^{2}:N,S-m^{2})]$  $pyS_{3}(\kappa^{2}:P,P-dppm)]Cl 1$ . Equimolar reaction of platinic acid (H<sub>2</sub>PtCl<sub>6</sub>) with pyridine-2-thione in toluene-ethanol mixture using Et<sub>3</sub>N as base followed by addition of one mole of dppm has also formed a mixed-ligand dinuclear complex  $[Pt^{I,II}_{2}(\mu-\kappa^{2}:N,S-pyS)_{3}(\mu-P,P-dppm)]Cl 4$ . Ethanol is known to reduce Pt<sup>IV</sup> of H<sub>2</sub>PtCl<sub>6</sub> to Pt<sup>II</sup> as observed earlier [45]. When PdCl<sub>2</sub>(dppm) was reacted with benzimidazoline-2-thione (bzimSH) in 1:1 or 1:2 molar ratios using the procedure adopted for 1, no product similar to 1 or cis-M( $\kappa^2$ :P,P-dppm)( $\kappa^1$ :S-L)<sub>2</sub> (A, Chart 2) could be established [12]. However, when benzimidazoline-2-thione was reacted with PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> in 2 : 1 molar ratio (L : M) in the presence of Et<sub>3</sub>N base in acetonitrile solvent, it has yielded mixed ligand complex,  $[Pd^{II}_{2}(\mu-\kappa^{2}:N,S-bzimS)_{2}(\kappa^{1}-S-bzimS)(PPh_{3})_{3}]Cl^{2}H_{2}O$  2, analogous to 1. A related ligand 6-methyl-1H-benzo[d]imidazole-2-thione(L) with Pd(II) has yielded a simple square planar complex,  $[PdCl_2(\kappa^1:S-L)(PPh_3)][56]$  Similarly, reaction of  $PdCl_2(PPh_3)_2$  with two moles of 1,3-imidazoline-2-thione in acetonitrile in presence of Et<sub>3</sub>N base did not form the expected dimer similar to 2, rather it has formed a square planar monomer,  $[Pd(\kappa^1:S-$ 

 $imzSH_2)_4]Cl_2 \cdot 2H_2O$  **3** involving de-ligation of PPh<sub>3</sub>. The difference in bonding of thio-ligands in complex **2** relative to complexes **1** and **4** is probably due to the higher steric requirement of benzimidazoline-2-thione which has not favored multiple bridging between two metals. Chart 3 shows bonding view of complexes synthesized.

The IR spectral data of complexes are given in the experimental section and that of the ligands is placed in supporting information. The IR spectrum of free pySH ligand shows a v(N-H) band at 3161 cm<sup>-1</sup> which is absent in its complexes **1** and **4**, and it showed deprotonation of the thio-ligand (pySH to pyS<sup>-</sup>). Similarly, the free pySH ligand showed a band at 1138 cm<sup>-1</sup> due to v(C=S) which is shifted to 1108, 1119 (**1**) and 1136 (**4**) cm<sup>-1</sup> in respective complexes. The v(N-H) band of free bzimSH at 3153 cm<sup>-1</sup> is absent in its complex **2**. The v(C=S) band at 1179 cm<sup>-1</sup> of free bzimSH is shifted to 1022 cm<sup>-1</sup> in complex **2**. In complex **3**, the v(N-H) band appeared at 3308 cm<sup>-1</sup> which is in the high energy region relative to the uncoordinated ligand (imzSH, 3130 cm<sup>-1</sup>). The characteristic v(C-S) band in complex **3** appears at 1119 cm<sup>-1</sup> and it remains unchanged relative to the free thio-ligand (1120 cm<sup>-1</sup>). The v(P-C<sub>Ph</sub>) peaks in the range, 1040-1098 cm<sup>-1</sup>, reveal the presence of coordinated phosphines in complexes. The IR spectra of complexes **2**, **3** and **4** have shown v(O-H) bands at 3393, 3384-3447 and 3453 cm<sup>-1</sup> respectively which confirm the presence of the non-bonded water molecules in complexes.

C



Chart 3. A view of bonding pattern of complexes synthesized.

#### 3.2. Molecular structures

Table 1 gives crystal data of compounds 1-4, while bond parameters are placed in Table 2. Complexes 1 and 2 formed monoclinic clinic crystals in space groups: C2/c and P2<sub>1</sub>/c respectively, while complexes 3 and 4 formed triclinic (3) or trigonal(4) crystals in space groups P-1 and P-3c1 respectively. Molecular structure of complex  $[Pd^{II}_2(\mu-\kappa^2:N, S-pyS)_3(dppm)]Cl 1$  is shown in Fig. 1. It has three anionic pyS<sup>-</sup> and one neutral dppm ligands which make N, S or P, P bridges between two metals. Each palladium metal is in divalent oxidation state and chloride is outside the coordination sphere of the cation  $[Pd^{II}_2(\mu-\kappa^2:N, S-pyS)_3(dppm)]^+$ . The Pd1 atom is bonded to two nitrogen atoms at Pd-N distances of 2.131(3), 2.075(3), one sulfur atom at Pd-S distance of 2.2901(10) and one phosphorus atom at Pd-P distance of 2.2614(11) Å (Table 2). The Pd2 atom is bonded to one nitrogen atom at Pd-N distance of 2.081(3), two sulfur atoms at Pd-S distances of 2.3052(10), 2.3517(11) and one phosphorus atom at Pd-P distance of 2.2843(11) Å. Thus the two metal centers have different coordination cores: PdN<sub>2</sub>PS and PdNPS<sub>2</sub>. The trans bond angles around the Pd1 and Pd2 metal centers, namely,  $[N(31)-Pd(1)-S(11), 175.77(10)^\circ$ , P(1)-Pd(1)-N(21) 173.29(9)°, S(31)-Pd(2)-N(11) 175.26(9)° and S(21)-Pd(2)-P(2) 175.84(4)°] deviate from linearity and it confirms that each of palladium centers has slightly distorted square

planar geometry. The Pd-S, Pd-N and Pd-P bond distances are similar to those found in reported complexes,  $[PdCl(\mu-\kappa^2: N,S-pymS)(PMe_3)]_2$  [48] and  $[PdCl(\mu-\kappa^2:N,S-pyS)(PMe_3)]_2$  [49]. The Pd-Pd distance of 2.7249(5) Å is less than the sum of van der Waals radius of palladium metal atom (3.20 Å) which suggests that there is a weak metal-metal interaction [57].



Fig. 1. ORTEP diagram of the molecule **1**  $[Pd_2(\mu - \kappa^2:N, S-pyS)_3(\kappa^2:P,P-dppm)]Cl$  at at 30% probability; hydrogens have been removed for clarity.

The coordination pattern and molecular structure of dinuclear complex,  $[Pt^{II}_2(\mu-\kappa^2: N, S-pyS)_3(\kappa^2:P,P-dppm)]Cl 4$  is similar to that of complex 1(Fig. 2). The Pt-S, Pt-N and Pt-P bond distances are similar to those found in reported complexes,  $[Pt_2(\mu-\kappa^2: N,S-pyS)_4]Cl_2$  [43] and  $[Pt(en)_2(\mu-\kappa^2: N,S-pyS)_2]Cl_2\cdot 3H_2O$  {en = ethylene diamine} [58]. The trans bond angles around the Pt1 and Pt2 metal centers deviate from linearity and it suggests that both the platinum metal centers have slightly distorted square planar geometries. The Pt-Pt distance of 2.7349(8) Å is less

than the sum of van der Waals radius of platinum metal atoms (3.40-3.60 Å) which suggests that there is a weak metal-metal bonding [57]



**Fig. 2.** ORTEP diagram of the molecule  $[Pt^{II}_{2}(\mu - \kappa^{2}: N, S-pyS)_{3}(\kappa^{2}:P,P-dppm)]Cl 4$ , at 30% probability. Hydrogens have been removed for clarity.

The bonding pattern of complex  $[Pd_2(\mu - \kappa^2: N, S-bzimS)_2(\kappa^1: S-bzimS) (PPh_3)_3]Cl 2H_2O 2$ is different from that of complex 1 due to different coordination modes adopted by benzimidazoline-2-thiolate anion (Fig.3). Here three anionic (bzimS<sup>-</sup>) and three PPh\_3 ligands coordinate to two metal centers and thio-ligands ligands are present in two different coordination modes: one of them is terminally S-bonded and other two thio-ligands are N,Sbridging. The Pd1 is bonded to one nitrogen atom at Pd-N distance of 2.058(3), one sulfur atom

at Pd-S distance of 2.3779(11) and two phosphorus atoms at Pd-P distances of 2.2992(12) and 2.3092(11) Å. The Pd2 is bonded to one nitrogen atom at Pd-N distance of 2.052(4), two sulfur atoms at Pd-S distances of 2.3669(11), 2.3140(12) and one phosphorus atom at Pd-P distance of 2.2744(11) Å. Thus two metal centers have different coordination cores: PdNP<sub>2</sub>S and PdNPS<sub>2</sub>. This complex **2** has two  $\mu$ -N,S bridging ligands with long Pd-Pd distance (4.371 Å) while complex **1** has three  $\mu$ -N,S bridging and one P,P-bridging ligands with short Pd-Pd distance of 2.7249(5) Å. The trans bond angles around metal centers fall in the range, 172 – 175° (approximately) (see Table 2) which deviate from linearity and hence the geometry around each metal center is distorted square planar similar to that observed in complex **1**.



Fig. 3. ORTEP diagram of  $[Pd_2(\mu-\kappa^2:N,S-bzimS)_2(\kappa^1:S-bzimS)(PPh_3)_3]^+$  cation of **2** at 30% probability; anion and hydrogens have been removed for clarity.

Finally the molecular structure of complex  $[Pd(\kappa^1:S-imzSH)_4]Cl_2 \cdot 2H_2O \ 3$  shown in Fig 4 is different from other three dinuclear complexes. Here Pd is coordinated to four sulfur atoms of neutral imidazoline-2-thione ligands. The trans S-Pd-S bond angles are 180° each with S1-Pd-S2 angles of 85.440(16) and 94.560(16)° and it suggests nearly square planar geometry arund the metal center. The Pd-S distances of 2.3305(4) and 2.3333(4) Å are very similar to the values, 2.336(2) and 2.327(1) Å reported for analogous complex,  $[Pd(\kappa^1:S-mimzSH)_4]Cl_2.2H_2O$  { mimzSH = 1-methylimidazoline-2-thione} [39].



**Fig. 4.** ORTEP diagram of molecule  $[Pd(\kappa^1:S-imzSH)_4]^{2+3}$  at 30% probability; chloride and water omitted for clarity

#### Table 1

Crystallographic data for complexes 1–4.

|                    | 1                             | 2                                 | 3                              | 4                             |
|--------------------|-------------------------------|-----------------------------------|--------------------------------|-------------------------------|
|                    |                               |                                   |                                | Ó                             |
| Empirical          | $C_{40}H_{34}ClN_3P_2Pd_2S_3$ | $C_{75}H_{65}ClN_6 P_3O_2Pd_2S_3$ | $C_{12}H_{20}Cl_2N_8O_2Pd S_4$ | $C_{40}H_{34}ClN_3P_2Pt_2S_3$ |
| formula            |                               |                                   |                                |                               |
| Μ                  | 963.07                        | 1518.67                           | 613.90                         | 1140.46                       |
|                    |                               |                                   | 5                              |                               |
| T /K               | 100 (2)                       | 173(2)                            | 123(2)                         | 293(2)                        |
| Crystal system     | Monoclinic                    | Monoclinic                        | triclinic                      | Trigonal                      |
| Space<br>group     | C 2/c                         | P 2 <sub>1</sub> /c               | P -1                           | P -3c1                        |
| a(Å)               | 17.2872(13)                   | 12.8539(6)                        | 8.0760(5)                      | 32.257(4)                     |
| b(Å)               | 15.7441(12)                   | 19.0643(9)                        | 8.2064(5)                      | 32.257(5)                     |
| c(Å)               | 32.164(2)                     | 28.5138(9)                        | 10.2050(6)                     | 19.126(6)                     |
| α (°)              | 90.00                         | 90.00                             | 68.311(5)                      | 90.00                         |
| β (°)              | 93.071(8)                     | 96.904(4)                         | 80.785(5)                      | 90.00                         |
|                    |                               |                                   |                                |                               |
| γ (°)              | 90.00                         | 90.00                             | 71.528(6)                      | 120.00                        |
| V(Å <sup>3</sup> ) | 8741.5 (11)                   | 6936.7(5)                         | 595.36(6)                      | 17235(8)                      |
| Z                  | 8                             | 4                                 | 1                              | 12                            |

| D <sub>calcd</sub>               | 1.464                       | 1.454                       | 1.712                       | 1.319                       |
|----------------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| $(g.cm^{-3})$                    |                             |                             |                             |                             |
| $\mu$ (mm <sup>-1</sup> )        | 1.131                       | 0.767                       | 1.380                       | 5.099                       |
| F(000)                           | 3880                        | 3096                        | 308                         | 6552                        |
| Reflections                      | 37294                       | 56438                       | 7208                        | 103125                      |
| Unique                           | 8525                        | 23285                       | 3918                        | 14727                       |
| reflections                      | (R <sub>int</sub> , 0.0293) | (R <sub>int</sub> , 0.0636) | (R <sub>int</sub> , 0.0246) | (R <sub>int</sub> , 0.1138) |
| Data/                            | 8525/ 0/ 469                | 23285/916/ 823              | 3918/ 0/ 141                | 14727/ 0/ 465               |
| restraints /                     |                             |                             |                             |                             |
| Reflens.wit h []> $2\sigma$ (J)] | 7035                        | 14056                       | 3315                        | 6753                        |
| R indices                        | $R_1 = 0.0392$              | 0.0690                      | 0.0267                      | 0.0685                      |
| [I>2o(I)]                        | wR <sub>2</sub> = 0.1025    | 0.1487                      | 0.0573                      | 0.1022                      |
| R indices                        | R1 = 0.0510                 | 0.1243                      | 0.0353                      | 0.1944                      |
| (all data)                       | wR <sub>2</sub> =0.1077     | 0.1781                      | 0.0592                      | 0.2324                      |
|                                  |                             |                             |                             |                             |
| Largest                          | 2.017 and                   | 1.498 and                   | 0.401 and                   | 2.563 and                   |
| diff. Peak<br>and hole           | -0.632 e.Å <sup>-3</sup>    | -1.561 e.Å <sup>-3</sup>    | -0.433 e.Å <sup>-3</sup>    | -1.501 e.Å <sup>-3</sup>    |
|                                  |                             |                             |                             |                             |

#### Table 2

#### Important bond lengths (Å) and angles (°) of complexes 1–4

| Compound 1  |            |             |            |
|-------------|------------|-------------|------------|
| Pd1-N31     | 2.075(3)   | Pd2-N11     | 2.081(3)   |
| Pd1-N21     | 2.131(3)   | Pd2-P(2)    | 2.2843(11) |
| Pd1–P1      | 2.2614(11) | Pd2-S31     | 2.3052(10) |
| Pd1-S11     | 2.2901(10) | Pd2-S21     | 2.3517(11) |
| Pd1–Pd2     | 2.7249(5)  | S21–C21     | 1.750(4)   |
| S11–C11     | 1.752(4)   | S31-C31     | 1.755(5)   |
| N21-Pd1-P1  | 173.29(9)  | N21-Pd1-S11 | 88.54(9)   |
| N31-Pd1-S11 | 175.77(10) | P1-Pd1-S11  | 85.23(4)   |
| N11-Pd2-S31 | 175.26(9)  | N31-Pd1-N21 | 92.54(13)  |
| P2-Pd2-S21  | 175.84(4)  | N31-Pd1-P1  | 93.86(10). |
| N11-Pd2-P2  | 94.73(9)   | P2-Pd2-S31  | 86.83(4)   |
| S31-Pd2-S21 | 89.09(4)   | N11-Pd2-S21 | 89.40(9)   |
| Compound 2  |            |             |            |
|             |            |             |            |
| Pd1-N21     | 2.058(3)   | Pd2         | 2.3140(12) |
| Pd1–P2      | 2.3092(11) | Pd2-S2      | 2.3669(11) |
| Pd1-P1      | 2.2992(12) | S1-C11      | 1.735(5)   |

| Pd1-S1   | 2.3774(11)   | S2-C21  | 1.728(5)   |
|--|--|---|--|
| Pd2-N11  | 2.052(4)   | S3–C31  | 1.713(5)   |
| Pd2-P3   | 2.2744(11)   |   | ~  |
| N21-Pd1-P1   | 172.57(9)  | P1-Pd1-S1   | 83.99(4)   |
| P2-Pd1-S1  | 174.16(4)  | N21-Pd1-S1  | 89.74(10)  |
| N11-Pd2-S3   | 175.08(10)   | P1–Pd1–P2   | 97.78(4)   |
| P3-Pd2-S2  | 174.84(4)  | N21-Pd1-P2  | 88.84(10)  |
| N11-Pd2-P3   | 91.36(9)   | S3–Pd2–S2   | 87.32(4)   |
| N11-Pd2-S2   | 93.80(9)   | P3-Pd2-S3   | 87.51(4)   |
| Compound 3 <sup>a</sup>  |  |   |  |
| <b>▲</b>   |  |   |  |
|  |  |   |  |
| Pd-S1  | 2.3305(4)  | S1-C11  | 1.7331(17)   |
| Pd-S1<br>Pd-S2   | 2.3305(4)<br>2.3333(4)   | S1-C11<br>S2-C21  | 1.7331(17)<br>1.7223(18)   |
| Pd-S1<br>Pd-S2<br>S1-Pd-S1   | 2.3305(4)<br>2.3333(4)<br>180.00   | S1-C11<br>S2-C21  | 1.7331(17)<br>1.7223(18)   |
| Pd-S1<br>Pd-S2<br>S1-Pd-S1<br>S1-Pd-S2                               | 2.3305(4)<br>2.3333(4)<br>180.00<br>85.440(16)                                     | S1-C11<br>S2-C21<br>S1-Pd-S2                            | 1.7331(17)<br>1.7223(18)<br>94.560(16)                                       |
| Pd–S1<br>Pd–S2<br>S1–Pd–S1<br>S1–Pd–S2                               | 2.3305(4)<br>2.3333(4)<br>180.00<br>85.440(16)                                     | S1-C11<br>S2-C21<br>S1-Pd-S2                            | 1.7331(17)<br>1.7223(18)<br>94.560(16)                                       |
| Pd–S1<br>Pd–S2<br>S1–Pd–S1<br>S1–Pd–S2<br>Compound 4                 | 2.3305(4)<br>2.3333(4)<br>180.00<br>85.440(16)                                     | S1-C11<br>S2-C21<br>S1-Pd-S2                            | 1.7331(17)<br>1.7223(18)<br>94.560(16)                                       |
| Pd-S1   Pd-S2   S1-Pd-S1   S1-Pd-S2   Compound 4   Pt1-N11           | 2.3305(4)<br>2.3333(4)<br>180.00<br>85.440(16)<br>2.045(9)                         | S1-C11<br>S2-C21<br>S1-Pd-S2<br>Pt2-N21                 | 1.7331(17)<br>1.7223(18)<br>94.560(16)<br>2.093(13)                          |
| Pd-S1   Pd-S2   S1-Pd-S1   S1-Pd-S2   Compound 4   Pt1-N11   Pt1-P2  | 2.3305(4)<br>2.3333(4)<br>180.00<br>85.440(16)<br>2.045(9)<br>2.255(3)             | S1-C11<br>S2-C21<br>S1-Pd-S2<br>Pt2-N21<br>Pt2-N31      | 1.7331(17)<br>1.7223(18)<br>94.560(16)<br>2.093(13)<br>2.072(11)             |
| Pd-S1   Pd-S2   S1-Pd-S1   S1-Pd-S2   Compound 4   Pt1-N11   Pt1-S21 | 2.3305(4)<br>2.3333(4)<br>180.00<br>85.440(16)<br>2.045(9)<br>2.255(3)<br>2.353(4) | S1-C11   S2-C21   S1-Pd-S2   Pt2-N21   Pt2-N31   Pt2-P1 | 1.7331(17)<br>1.7223(18)<br>94.560(16)<br>2.093(13)<br>2.072(11)<br>2.239(4) |



<sup>a</sup> Symmetry operators used: -x, -y, -z

#### 3.3 Electronic absorption/ emission and NMR spectroscopy

Complexes 1, 3 and 4 have shown weak to intense electronic absorption bands with vibronic fine structure in the region 265-422 nm (Fig. 5). The intense absorption bands in the region 265-340 nm are due to intra-ligand transitions  $(\pi \rightarrow \pi^*/ n \rightarrow \pi^*)$ . Further, the absorption bands in the region, 354-441 nm are attributed to LLCT (ligand to ligand charge transfer) and MLCT (metal to ligand charge transfer) bands. It may be noted that similar type of assignments have been made in literature for the dinuclear complexes,  $[M_2(dtbpy)_2(\mu-\kappa^2:N,S-pyS)_2][ClO_4]_2$ (M = Pt or Pd; dtbpy = 4, 4'-di-tert-butyl-2,2'-bipyridine) [59]. In order to check the emission property, the complexes were excited in the region 320 to 360 nm and complexes have shown intense emission bands in the 360-600 nm region with  $\lambda_{max}$  at 422 to 442 nm (Fig. 6). The emission bands are attributed to the transitions from excited state of ligands ( $\pi^*$ ) to the ground state of ligands ( $\pi$ ) [LLCT] or and transition from excited state of ligand ( $\pi^*$ ) to ground state of metal ( $d\sigma^*$ ,  $dz^2$ ) orbital [LMCT]. These transitions are assigned on a pattern similar to that reported in literature [59].



Fig. 5. Electronic absorption spectra of complexes 1, 3 and 4.



**Fig. 6.** Fluorescence spectra of complexes 1 ( $\lambda_{max}^{em} = 442 \text{ nm}$ ,  $\lambda_{max}^{ex} = 322 \text{ nm}$ ), 3 ( $\lambda_{max}^{em} = 442 \text{ nm}$ ,  $\lambda_{max}^{ex} = 342 \text{ nm}$ ) and 4 ( $\lambda_{max}^{em} = 439 \text{ nm}$ ,  $\lambda_{max}^{ex} = 358 \text{ nm}$ ).

The <sup>1</sup>H NMR spectra of complexes,  $[Pd_2(\mu - \kappa^2:N, S-pyS)_3(\kappa^2:P,P-dppm)]Cl 1$ ,  $[Pd(\kappa^1:S-imzSH)_4]Cl_2 \cdot 2H_2O 3$ , and  $[Pt_2(\mu - \kappa^2:N,S-pyS)_3(\kappa^1:P,P-dppm)]Cl 4$ , has been recorded. Complex 1 did not show the presence of NH proton signals ( $\delta = 13.40$  ppm, free pySH ligand) suggesting that the thio ligands are coordinating to the metal center as mono anions (pyS<sup>-</sup>). The pyridyl group of a thio ligand shows more than one signal due to each of H<sup>6</sup>, H<sup>3</sup>, H<sup>4</sup>, and H<sup>5</sup> protons which reveal difference in chemical environment of pyridyl groups in the mixed valent complex. The H<sup>6</sup> and H<sup>3</sup> protons showed the highest low field shifts and support coordination of nitrogen and sulfur donor atoms to the metal centers. The H<sup>4</sup> and H<sup>5</sup> proton signals also move downfield in the complex. The low field shifts in pyridyl proton signals of complex **4** are somewhat lower than those shown by complex **1** (see experimental). The phenyl protons of dppm in complexes **1** and **4** appeared as resolved multiplets for o-, p- and m-H at  $\delta = 7.69-7.70$ , 7.14-7.37, 6.91-7.27 ppm respectively. The -CH<sub>2</sub>- protons appeared as two separate sets of multiplets at  $\delta$  4.24 and 4.41; 4.33 and 4.66 ppm for complexes **1** and **4** respectively. The NMR spectrum of complex **2** 

could not be recorded due to due to its poor solubility. The NH ( $\delta = 11.93$  ppm) and ring protons (H<sup>4</sup>, H<sup>5</sup>,  $\delta = 7.25$  ppm) of imidazoline ring in complex **3** moved high field relative to the free ligand (NH proton,  $\delta = 12.17$  ppm, H<sup>4</sup>, H<sup>5</sup>  $\delta = 7.28$  ppm). The <sup>31</sup>P NMR spectrum of complex **1** shows two <sup>31</sup>P NMR signals at  $\delta = 32.46$  ppm, (J<sub>p-p</sub> = 61.5 Hz) and 28.02 ppm (J<sub>p-p</sub> = 60 Hz) corresponding to two different types of phosphorus atoms. Similarly, <sup>31</sup>P NMR spectrum of complex **4** also shows two <sup>31</sup>P NMR signals at  $\delta = 12.70$  (J<sub>p-p</sub> = 38.9 Hz) ppm and 8.29 (J<sub>p-p</sub> = 38.9 Hz) ppm. The presence of two sets of <sup>31</sup>P NMR signals could be due to non equivalent environment around the phosphorus atoms (Figs. 7 and 8). The lack of satellites due to <sup>195</sup>Pt nucleus with I = 1/2 is due to the low abundance of <sup>195</sup>Pt.



**Fig. 7.** <sup>31</sup>P NMR spectrum of  $[Pd_2(\mu - \kappa^2: N, S-pyS)_3(dppm)]Cl 1$ .



Fig. 8. <sup>31</sup>P NMR spectrum of  $[Pt_2(\mu - N, S-pyS)_3(\kappa^2:P,P-dppm)]Cl$  4.

#### 3.4. ESI Mass spectral studies

ESI-mass spectral data of complexes (1, 3, 4) have been obtained. The purpose of carrying out this study was to determine the molecular ion  $([M]^+)$ , to understand the fragmentation pattern and formation of new species, if any. Complexes 1 and 4 showed the presence of the molecular species,  $[M]^+$  (1 : m/z obsd. 925.95; calcd. 925.94); (4 : m/z obsd. 1104.13; calcd.1104.07) (Figs. 9 and 10). Fig. 11 reveals ESI-mass peak due to  $[Pd(imzSH)_3Cl]^+$  species (3 : m/z obsvd 440.93, m/z calcd. 440.90) and its isotopic pattern. A few other species are placed in supplementary.



**Fig. 9.** ESI-mass peak due to the species  $[Pd_2(pyS)_3(dppm)]^+$ , m/z observed 925.95, m/z calcd. 925.94 with isotopic pattern (complex 1)



**Fig. 10**. ESI-mass peak due to the species  $[Pt_2(pyS)_3dppm]^+$ , m/z observed 1104.13, m/z calcd. 1104.07 with isotopic pattern (complex 4)



Fig. 11. ESI-mass peak due to  $[Pd(imzSH)_3Cl]^+$  species, m/z observed 440.93, m/z calcd. 440.90 with isotopic pattern (complex 3)

#### 4. Conclusion

Three mixed-ligands dinuclear complexes, namely,  $[Pd^{II}_{2}(\mu-\kappa^{2}:N,S-pyS)_{3}(\mu-P,P-dppm)]Cl$ **1**,  $[Pd^{II}_{2}(\mu-\kappa^{2}:N,S-bzimS)_{2}(\kappa^{1}-S-bzimS)(PPh_{3})_{3}]Cl\cdot2H_{2}O$  **2** and  $[Pt^{II}_{2}(\mu-\kappa^{2}:N,S-pyS)_{3}(\mu-P,P-dppm)]Cl$  **4**, have been synthesised ( $pyS^{-} = pyridine-2$ -thiolate;  $bzimS^{-} = benzimidazoline-2$ -thiolate; dppm =  $Ph_{2}P-CH_{2}-PPh_{2}$ ). Using a different procedure, equimolar reaction of  $[PdCl_{2}(dppm)]$  with sodium salt of pyridine-2-thiolate in ethanol also gave a  $Pd^{II}-Pd^{II}$  dimer,  $[Pd_{2}(\mu-\kappa^{2}:N, S-pyS)_{3}(\kappa^{2}: P,P-dppm)]\cdotCl$  [14]. The difference in bonding of thio-ligands in complex **2** relative to complexes **1** and **4** is probably due to the higher steric requirement of benzimidazoline-2-thiolate anion which has not favored multiple bridging between two metals. Complexes **1**, **3** and **4** have shown intense fluorescence. ESI mass studies of **1** and **4** have supported the formation of the molecular species,  $[Pd_{2}(pyS)_{3}(dppm)]^{+}$  and  $[Pt_{2}(pyS)_{3}(dppm)]^{+}$ 

#### Supplementary material

CCDC, 1426481(1), 1426482 (2), 1426483 (3) and 1426484 (4) contain the supplementary crystallographic data for complexes 1-4 respectively of this paper. 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; mail: <u>deposit@ccdc.cam.ac.uk</u>. supporting information: spectroscopic data of ligands; ESI-mass data of complexes.

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## **Synopsis**

Three mixed-ligand dinuclear complexes, namely,  $[Pd^{II}_{2}(\mu-\kappa^{2}:N,S-pyS)_{3}(\mu-P,P-dppm)]Cl$  **1**,  $[Pd^{II}_{2}(\mu-\kappa^{2}:N,S-bzimS)_{2}(\kappa^{1}-S-bzimS)(PPh_{3})_{3}]Cl\cdot 2H_{2}O$  **2** and  $[Pt^{II}_{2}(\mu-\kappa^{2}:N,S-pyS)_{3}(\mu-P,P-dppm)]Cl$  **4** synthesized are fluorescent. ESI mass studies also support formation of molecular ion species,  $[M_{2}(pyS)_{3}(dppm)]^{+}$ .

