

# Oxidative addition of disulfide/diselenide to group 10 metal(0) and *in situ* functionalization to form neutral thiasalen/selenasalen group 10 metal(II) complexes†

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Three components, one pot synthesis of thiasalen/selenasalen Ni(II), Pd(II) and Pt(II) complexes, **14–19**, by the oxidative addition of S–S/Se–Se bond of bis(*o*-formylphenyl)disulfide/-diselenide to Ni(0), Pd(0) and Pt(0) followed by *in situ* Schiff base formation with ethylenediamine is reported. S–S or Se–Se bonds were cleaved and coordinated to the metal center as thiolate (ArS<sup>−</sup>) or selenolate (ArSe<sup>−</sup>) while the formal oxidation state of metal centers was changed from '0' to '+2'. The disulfide/diselenide reacted with zero-valent metals at room temperature to give only the monometallic complexes. All complexes (except Pd–thiolate complex **15**) were studied by single crystal X-ray crystallography and revealed the square planar geometry around metal centers.

## Introduction

Schiff base synthesized by the reaction of two equivalents of salicylaldehyde with one equivalent of ethylenediamine is known as 'salen' which provides potentially tetradentate chelating systems with a N<sub>2</sub>O<sub>2</sub> donor set. Metal complexes based on salen and its derivatives have drawn considerable attention in last few decades<sup>1</sup> due to their applications in catalysis, biological studies, material science, molecular magnetism and sensory materials.<sup>2</sup> As catalysts, such complexes have been successfully applied in many reactions such as oxidation, olefin epoxidation, cycloaddition and in asymmetric synthesis.<sup>3</sup> Recently, salen-complexes were utilized to develop metal organic frameworks (MOFs) for their novel applications such as hydrogen gas storage and highly efficient catalysis.<sup>4</sup> Sulfur and selenium analogues of salen (thiasalen and selenasalen with N<sub>2</sub>S<sub>2</sub> and N<sub>2</sub>Se<sub>2</sub> ligating sites) have attracted scant attention due to instability of thiol and selenol groups compared to the hydroxyl group of salen.

Oxidative addition of E–E bonds (E = S and Se) of diorganodisulfides and -diselenides to low-valent transition metal complexes is a mild and efficient method to synthesize

chalcogenolato-metal complexes.<sup>5</sup> The oxidative addition of diorganyl disulfides/diselenides to Pd(0) complexes, such as [Pd(PPh<sub>3</sub>)<sub>4</sub>], was investigated for their addition to alkynes, which is an efficient single step method for the formation of two C–S/Se bonds in a stereoselective manner.<sup>6</sup> Mechanistic studies on these reactions have been carried out using various types of disulfides/diselenides and alkynes from both the experimental and theoretical point of views.<sup>7</sup> Yamamoto and Sekine have reported the oxidative addition of diaryl disulfides, ArS–SAr, with [Ni(COD)<sub>2</sub>] (COD = 1,5-cyclooctadiene) in the presence of basic ligands such as 2,2'-bipyridine, triethylphosphine.<sup>8</sup> Oxidative addition of diaryl disulfides (ArS)<sub>2</sub> with [Pd(PPh<sub>3</sub>)<sub>4</sub>] and [Pt(PPh<sub>3</sub>)<sub>4</sub>] formed dimeric and monomeric complexes, respectively.<sup>9</sup> The tendency of formation of dimeric complexes can be minimized by using electron withdrawing substituents on the aromatic rings of diaryl disulfide. This study also revealed that Pt(0) complexes have less tendency to form dimeric complexes compared to Pd(0) precursors. The oxidative addition of S–S bond of the ring systems to Ni(0), Pd(0) and Pt(0) to form *S,S*-dithiolate chelate complexes were also studied.<sup>10</sup>

Morley *et al.*<sup>11</sup> have shown the formation of selenolate complexes *via* oxidative addition of Ph<sub>2</sub>Se<sub>2</sub> and Fc<sub>2</sub>Se<sub>2</sub> [Fc = ferrocenyl] to Pd(0) and Pt(0). Laitinen *et al.* reported the oxidative addition of Th<sub>2</sub>Se<sub>2</sub> and Ph<sub>2</sub>Se<sub>2</sub> to Pd(0) and Pt(0).<sup>12</sup> Reversible oxidative addition of Se–Se bonds to Pt(0) and Pt(II) precursors was observed by changing the ligand environment.<sup>13</sup> However, oxidative addition of Se–Se bond of diorganodiselenide to Ni(0) is not reported till the date. In addition to oxidative

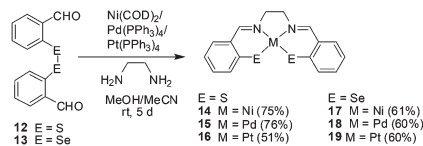
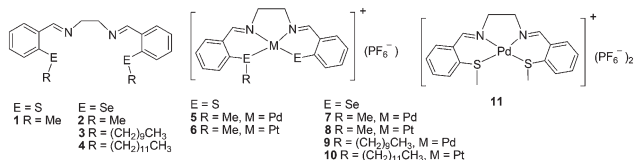
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† Electronic supplementary information (ESI) available: <sup>1</sup>H, <sup>13</sup>C and <sup>77</sup>Se spectra of complexes **14–19**. CCDC 946622–996626. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt52132j



addition of E–E bonds to group 10 M(0) precursors, the cleavage of E–E bonds also have also been reported with Group 10 metals in higher oxidation states.<sup>14</sup>

Synthesis of ligands and complexes simultaneously by the formation of both carbon–heteroatom and heteroatom–metal bonds is a powerful technique in the preparation of metallo-organic self assemblies.<sup>15</sup> The introduction of thiolates/selenolates into metal complexes directly by the oxidative addition of dichalcogenides are often complicated by the presence of dimeric/polynuclear and non-stoichiometric compounds, however, it can be avoided by using the chelating diselenide.<sup>5a</sup> Here we have used this approach to synthesize thiasalen and selenasalen complexes.

Earlier we reported the Pd(II) and Pt(II) complexes (5–11) which were prepared by the reactions of bis(alkyl)thiasalen (1) and bis(alkyl)selenasalen (2–4) ligands with Pd(II) and Pt(II) metal precursors.<sup>16</sup> We have observed dealkylative complexation *via* nucleophilic substitution at C–E bond (E = S, Se) where monocationic complexes act as a leaving groups. However, the attempts to prepare the analogous Ni(II) complexes were unsuccessful. In the synthesis of complexes 5–11, the two step process was applied; (i) synthesis and isolation of the ligand and then (ii) complexation with the metal precursors. Here we report the complete series of six neutral group 10 d<sup>8</sup> metal complexes of thia/selenasalen ligands *via* oxidative addition of E–E bond of bis(orthoformyl)phenyl disulfide (12) and bis(orthoformyl)phenyl diselenide (13) to Ni(0), Pd(0) and Pt(0) and subsequent *in situ* reaction of ethylene diamine. Thus it is a three component one pot reaction for facile synthesis of sulfur and selenium analogues of salen group 10 metal complexes. It is the first report on the synthesis of neutral thiasalen complexes of Pd and Pt and selenasalen complexes of Ni, Pd and Pt.



Scheme 1 Synthesis of complexes 14–19.

and coordinated to the metal center as thiolate (ArS<sup>−</sup>) or selenolate (ArSe<sup>−</sup>) while the formal oxidation state of metal center was changed from '0' to '+2'. The intermediate aldehyde complexes were used *in situ* as template for the preparation of desired Schiff base derivatives. Thus, it provides a one pot three component method for synthesis of the thiasalen and selenasalen d<sup>8</sup> metal complexes by template synthesis using oxidative addition of bis(*o*-formylphenyl)disulfide/diselenide to M(0) (M = Ni, Pd, Pt) precursors and imine bond formation by reaction with ethylenediamine. Template synthesis is a well established method for the one pot synthesis of Schiff-base complexes. In the template synthesis method a metal ion first coordinates with aldehyde to create the template for the reaction with amine to form metal ion coordinated Schiff-base.<sup>19</sup> Thus, the concept of simultaneous use of oxidative addition and template synthesis is used here for one pot synthesis of thiasalen/selenasalen based metal complexes.

When one equivalent of ligand 12 was treated with one equivalent of [Ni(COD)<sub>2</sub>], [Pd(PPh<sub>3</sub>)<sub>4</sub>] and [Pt(PPh<sub>3</sub>)<sub>4</sub>] and one equivalent of 1,2-ethylenediamine, complexes 14, 15 and 16 were formed, respectively. All the three complexes are red in colour and stable in solid as well as in solution phase at ambient conditions. Complex 14 is soluble in DCM, CHCl<sub>3</sub>, DMF and DMSO while complexes 15 and 16 are soluble in DMF and DMSO. Previously, Yamamura *et al.*<sup>20</sup> reported the synthesis of complex 14 by the reaction of bis(2-(*tert*-butylthio)benzylidene)ethylenediamine with NiCl<sub>2</sub>·6H<sub>2</sub>O with *in situ* cleavage of *tert*-butyl group. Goswami and Eichhorn<sup>15</sup> reported the synthesis of 14 by the cleavage of disulfide bond in bis(*o*-formylphenyl)disulfide using [Ni(en)<sub>3</sub>]Cl<sub>2</sub>. In both the cases, Ni(II) ion was taken as metal source. Elemental analysis data of the compounds 14, 15 and 16 are consistent with the proposed formula and structures. <sup>1</sup>H/<sup>13</sup>C NMR spectra of the complexes 14, 15 and 16 are in good agreement with the proposed structures. <sup>1</sup>H NMR spectra of the complexes 14, 15 and 16 showed a singlet at δ 8.59, 8.72 and 9.02 ppm for azomethine protons, respectively. Complexes 14, 15 and 16 showed eight signals in the <sup>13</sup>C NMR spectra for eight different types of carbons indicating symmetrical nature of the complexes in solution. FT-IR spectra of the complexes 14, 15 and 16 displayed the characteristic ν(C=N) stretching frequencies at 1610, 1626 and 1617 cm<sup>−1</sup>, respectively, which were shifted to lower energy values compared to the ν(C=O) stretching frequency (1691 cm<sup>−1</sup>) of precursor 12.

The selenium analogues 17, 18 and 19 were prepared by similar procedure using precursor bis(orthoformylphenyl) diselenide 13. Formulations of complexes 17–19 were supported by elemental analyses, however, elemental analysis for 18 was

## Result and discussion

### Synthesis of ligands

The compounds 12<sup>17</sup> and 13<sup>18</sup> were synthesized according to the reported procedures. <sup>1</sup>H NMR spectrum of the ligand 12 showed a singlet at δ 10.23 ppm for aldehyde protons whereas for ligand 13 showed a singlet at δ 10.17 ppm.

### Complexation of compound 12 and 13 with Ni(0), Pd(0) and Pt(0)

Reactions of ligands 12 and 13 with Ni(0) ([Ni(COD)<sub>2</sub>]), Pd(0) ([Pd(PPh<sub>3</sub>)<sub>4</sub>]) and Pt(0) ([Pt(PPh<sub>3</sub>)<sub>4</sub>]) afforded six neutral thiolate and selenolate complexes 14–19 *via* oxidative addition of E–E bond (E = S, Se) to Ni(0), Pd(0) and Pt(0) at room temperature (Scheme 1). As a result, S–S or Se–Se bonds were cleaved



found to be slightly deviated from the calculated value of percentage of carbon. Color, stability and solubility of these complexes are quite similar to that of their sulfur analogues.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of **17**, **18** and **19** showed symmetrical nature of these complexes. The characteristic imine protons were observed at  $\delta$  8.66, 8.76 and 9.09 ppm, respectively, in  $^1\text{H}$  NMR spectra of **17**, **18** and **19**.  $^{77}\text{Se}$  NMR of complexes **17**, **18**, **19** showed the single resonance at  $\delta$  354.9, 393.7, 318.9 ppm, respectively. In the FT-IR spectra of complexes **17**, **18** and **19**, peaks at 1609, 1622 and 1611  $\text{cm}^{-1}$ , respectively, were assigned to  $\nu_{(\text{C}=\text{N})}$  stretching frequency. ESI-MS spectra of complexes **14** and **17** displayed the molecular ion peak at 356.37 and 452.1934, respectively as  $[\text{M} + \text{H}]^+$  moieties, while the Pd(II) and Pt(II) complexes did not ionize in ESI mass spectrometer.

### Crystal structure study

The molecular structures and supramolecular assemblies of **14**, **16**, **17**, **18** and **19** have been determined by X-ray crystallography.

#### Crystal structure of Ni–thiolate complex **14**

Complex **14** crystallizes in orthorhombic space group  $Pna2_1$  with the square planar geometry around metal center (Fig. 1). Space group, unit cell and bond lengths/angles are quite similar to those reported by Yamamura *et al.*,<sup>20</sup> while Goswami and Eichhorn<sup>15</sup> reported the monoclinic space group  $P2_1/c$  with asymmetric unit containing two independent molecules and a dichloromethane molecule.

#### Crystal structure of Pt–thiolate complex **16**

Complex **16** crystallizes in the monoclinic space group  $P2_1/c$  with a square planar geometry around the Pt(II) center (Fig. 2). The two Pt–S bonds are nearly equal and slightly shorter than

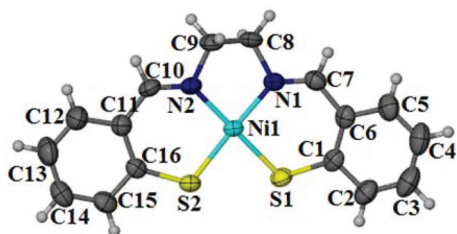


Fig. 1 ORTEP representation of nickel complex **14**; thermal ellipsoids are drawn at 50% probability level.

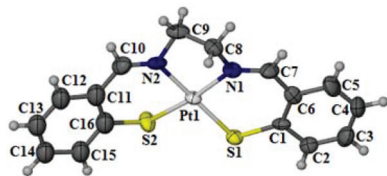


Fig. 2 ORTEP representation of platinum complex **16**; thermal ellipsoids are drawn at 50% probability level.

Table 1 Selected bond lengths (Å) and angles (°) for **16**

| S. no | Bond lengths (Å) |           | Bond angles (°) |           |
|-------|------------------|-----------|-----------------|-----------|
| 1     | Pt1–S1           | 2.246(4)  | S1–Pt1–S2       | 89.53(16) |
| 2     | Pt1–S2           | 2.225(4)  | N1–Pt1–N2       | 82.4(6)   |
| 3     | Pt1–N1           | 2.025(14) | S1–Pt1–N2       | 176.6(4)  |
| 4     | Pt1–N2           | 2.039(13) | S2–Pt1–N1       | 173.2(4)  |
| 5     | S1–C1            | 1.760(16) | S1–Pt1–N1       | 95.7(4)   |
| 6     | S2–C16           | 1.83(2)   | S2–Pt1–N2       | 92.6(4)   |

that in thioether–thiolate complex **12** (thioether Pt–S, 2.2614(7) Å and thiolate Pt–S, 2.2539(7) Å), respectively.<sup>16b</sup> Selected bond lengths and bond angles are shown in Table 1. Crystal packing of complex **16** shows the formation of 2D sheet along  $bc$  plane via C–H $\cdots\pi$  (H1A $\cdots$ C1–C6), H5 $\cdots$ H14 and H1A $\cdots$ S1 interactions (Fig. S1 $\dagger$ ). Intermolecular S1 $\cdots$ H2B and H5 $\cdots$ H14 interactions present in the crystal lattice construct the two dimensional sheet along  $ac$  plane (Fig. S2 $\dagger$ ).

#### Crystal structure of Ni–selenolate complex **17**

The square planar geometry around Ni(II) center in complex **17** was confirmed by single crystal X-ray crystallography. Complex **17** crystallizes in triclinic space group  $P\bar{1}$  with two asymmetric molecules in the unit cell (Fig. 3). The four Ni–Se bonds are nearly equal (average 2.263 Å) and comparable to those reported for selenocarbamoyl benzamidine base Ni(II) complex (2.278 and 2.293 Å)<sup>21</sup> and 2-aminophenyl diselenolate based Ni(II) complex (2.295 Å)<sup>22</sup> which also have square planar geometry around the Ni(II) center with N2Se2 donor set. The average Ni–N bond distance is 1.894 Å. The various intermolecular nonbonding interactions including CH $\cdots\pi$  (aromatic) interaction between the two molecules led to the formation of 1-D chain along  $b$  axis (Fig. S3 $\dagger$ ). Selected bond lengths and bond angles are shown in Table 2.

#### Crystal structure of Pd–selenolate complex **18**

Similar to complex **17**, the crystal structure of complex **18** crystallizes in the triclinic space group  $P\bar{1}$  with two molecules in the asymmetric unit ( $Z = 4$ ,  $Z' = 2$ ) and a square planar

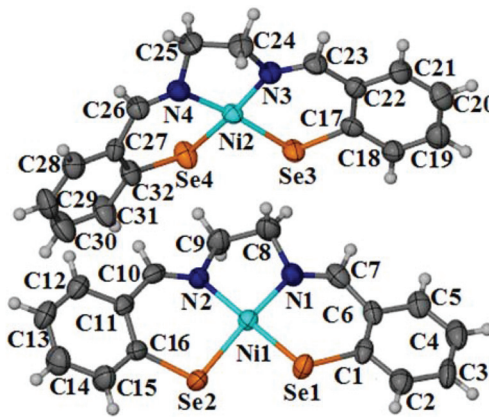
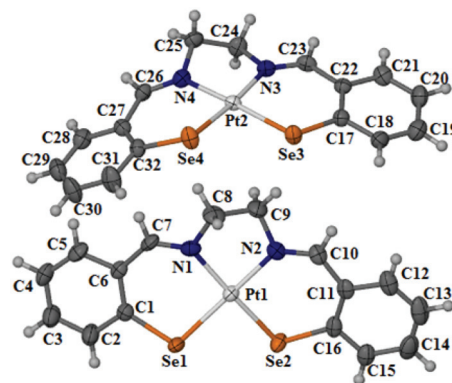
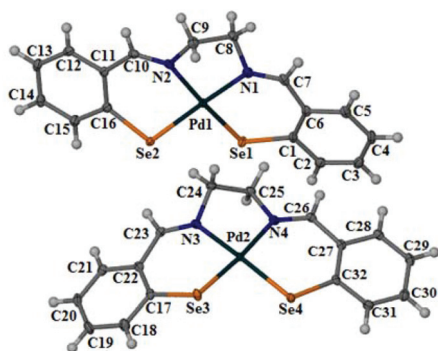


Fig. 3 ORTEP representation of platinum complex **17**; thermal ellipsoids are drawn at 50% probability level.



**Table 2** Selected bond lengths (Å) and bond angles (°) for complex 17

| S. no | Bond lengths (Å) |            | Bond angles (°) |            |
|-------|------------------|------------|-----------------|------------|
| 1     | Ni1–Se1          | 2.2576(13) | Se1–Ni1–Se2     | 83.60(5)   |
| 2     | Ni1–Se2          | 2.2578(13) | Se3–Ni2–Se4     | 84.03(4)   |
| 3     | Ni2–Se3          | 2.2860(13) | N1–Ni1–N2       | 86.9(2)    |
| 4     | Ni2–Se4          | 2.2518(13) | N3–Ni2–N4       | 86.52(19)  |
| 5     | Ni1–N1           | 1.897(4)   | Se1–Ni1–N2      | 171.68(14) |
| 6     | Ni1–N2           | 1.887(5)   | Se2–Ni1–N1      | 171.53(14) |
| 7     | Ni2–N3           | 1.896(5)   | Se2–Ni1–N2      | 95.99(15)  |
| 8     | Ni2–N4           | 1.894(4)   | Se1–Ni1–N1      | 94.73(15)  |
| 9     | Se1–C1           | 1.902(3)   | Se3–Ni2–N3      | 93.10(13)  |
| 10    | Se2–C16          | 1.887(3)   | Se3–Ni2–N4      | 172.87(15) |
| 11    | Se3–C17          | 1.890(3)   | Se4–Ni2–N3      | 172.33(16) |
| 12    | Se4–C32          | 1.898(3)   | Se4–Ni2–N4      | 97.20(14)  |

**Fig. 5** ORTEP representation of palladium complex 19; thermal ellipsoids are drawn at 50% probability level.**Fig. 4** ORTEP representation of palladium complex 18; thermal ellipsoids are drawn at 50% probability level.

geometry around the Pd(II) centers (Fig. 4). The average distance of four Pd–Se bonds is 2.366 Å which is slightly shorter than Pd–Se bonds of nicotinoyl selenide based square planar Pd(II) complex (2.444 and 2.428 Å).<sup>23</sup> The average of four Pd–N bond distances is 2.036 Å. Selected bond lengths and bond angles are shown in Table 3. Crystal packing of 18 shows the intermolecular C–H... $\pi$ ,  $\pi$ ... $\pi$  and Se...H short contacts (Fig. S4†).

### Crystal structure of Pt–selenolate complex 19

Complex 19 crystallizes in the triclinic space group  $P\bar{1}$  with two molecules in the asymmetric unit ( $Z = 4$ ,  $Z' = 2$ ) and a square

**Table 3** Selected bond lengths (Å) and angles (°) for 18

| S. no | Bond lengths (Å) |            | Bond angles (°) |            |
|-------|------------------|------------|-----------------|------------|
| 1     | Pd1–Se1          | 2.3587(3)  | Se1–Pd1–Se2     | 87.281(10) |
| 2     | Pd1–Se2          | 2.3639(3)  | Se3–Pd2–Se4     | 87.796(10) |
| 3     | Pd2–Se3          | 2.3809(3)  | N1–Pd1–N2       | 84.44(7)   |
| 4     | Pd2–Se4          | 2.3588(3)  | N3–Pd2–N4       | 83.60(7)   |
| 5     | Pd1–N1           | 2.0328(18) | Se1–Pd1–N2      | 173.09(5)  |
| 6     | Pd1–N2           | 2.0358(18) | Se2–Pd1–N1      | 173.30(5)  |
| 7     | Pd2–N3           | 2.0344(19) | Se2–Pd1–N2      | 94.02(5)   |
| 8     | Pd2–N4           | 2.0390(17) | Se1–Pd1–N1      | 95.02(5)   |
| 9     | Se1–C1           | 1.893(2)   | Se3–Pd2–N3      | 92.60(5)   |
| 10    | Se2–C16          | 1.899(2)   | Se3–Pd2–N4      | 174.89(5)  |
| 11    | Se3–C17          | 1.898(2)   | Se4–Pd2–N3      | 175.76(5)  |
| 12    | Se4–C32          | 1.895(2)   | Se4–Pd2–N4      | 96.24(5)   |

**Table 4** Selected bond lengths (Å) and angles (°) for 19

| S. no | Bond lengths (Å) |           | Bond angles (°) |            |
|-------|------------------|-----------|-----------------|------------|
| 1     | Pt1–Se1          | 2.3641(7) | Se1–Pt1–Se2     | 87.08(3)   |
| 2     | Pt1–Se2          | 2.3731(7) | Se3–Pt2–Se4     | 87.58(2)   |
| 3     | Pt2–Se3          | 2.3866(7) | N1–Pt1–N2       | 83.3(2)    |
| 4     | Pt2–Se4          | 2.3672(7) | N3–Pt2–N4       | 83.2(2)    |
| 5     | Pt1–N1           | 2.017(5)  | Se1–Pt1–N2      | 174.44(15) |
| 6     | Pt1–N2           | 2.015(6)  | Se2–Pt1–N1      | 174.43(15) |
| 7     | Pt2–N3           | 2.027(5)  | Se2–Pt1–N2      | 94.55(16)  |
| 8     | Pt2–N4           | 2.020(5)  | Se1–Pt1–N1      | 95.53(17)  |
| 9     | Se1–C1           | 1.883(7)  | Se3–Pt2–N3      | 93.28(15)  |
| 10    | Se2–C16          | 1.900(7)  | Se3–Pt2–N4      | 174.95(15) |
| 11    | Se3–C17          | 1.895(6)  | Se4–Pt2–N3      | 175.96(15) |
| 12    | Se4–C32          | 1.882(6)  | Se4–Pt2–N4      | 96.20(15)  |

planar geometry around the Pt(II) centre (Fig. 5). The four Pt–Se bonds are nearly equal and comparable to those in selenoether–selenolate complex 8 (selenoether Pt–Se, 2.3636(6) Å and selenolate Pt–Se, 2.3583(6) Å).<sup>16a</sup> The average Pt–N bond distance is 2.019 Å. Selected bond lengths and bond angles are shown in Table 4. Molecular packing of the complex is similar to that of nickel and palladium analogues.

Complete crystallographic data for complex 14, 16–19 are provided in Table 5.

## Conclusion

In summary, the reactions of ligands bis(*o*-formylphenyl)disulfide/diselenide (12 and 13) with [Ni(COD)<sub>2</sub>], [Pd(PPh<sub>3</sub>)<sub>4</sub>] and [Pt(PPh<sub>3</sub>)<sub>4</sub>] afforded six neutral square planar thiolate and selenolate complexes 14–19 via oxidative addition of E–E bond (E = S, Se) to Ni(0), Pd(0) and Pt(0) followed by imine bond formation by reaction with ethylene diamine. Thus we developed three-component (group 10 M(0) precursor, bis(*o*-formylphenyl)disulfide/diselenide, and ethylene diamine), one-pot reaction for the synthesis of thiasalen and selenasalen group 10 metal complexes. We believe that the reaction can be extended to the various derivatives of complexes 14–19 by using substituted bis(*o*-formylphenyl)disulfide/diselenide and



Table 5 Crystallographic information of complex 14, 16, 17, 18 and 19

| Formula                                     | C <sub>16</sub> H <sub>14</sub> N <sub>2</sub> NiS <sub>2</sub> | C <sub>16</sub> H <sub>14</sub> N <sub>2</sub> PtS <sub>2</sub> | C <sub>16</sub> H <sub>14</sub> N <sub>2</sub> NiSe <sub>2</sub>  | C <sub>16</sub> H <sub>14</sub> N <sub>2</sub> PdSe <sub>2</sub>  | C <sub>16</sub> H <sub>14</sub> N <sub>2</sub> PtSe <sub>2</sub> |
|---|---|---|---|---|--|
| Crystal system                              | Orthorhombic  | Monoclinic  | Triclinic   | Triclinic   | Triclinic  |
| Space group                                 | <i>Pna</i> 2(1)   | <i>P</i> 2 <sub>1</sub> / <i>c</i>                              | <i>P</i> $\bar{1}$  | <i>P</i> $\bar{1}$  | <i>P</i> $\bar{1}$   |
| <i>a</i> [Å]                                | 8.9500(7)   | 7.5651(9)   | 10.398(6)   | 10.3810(10)   | 10.4940(12)  |
| <i>b</i> [Å]                                | 22.688(2)   | 7.9224(9)   | 12.088(7)   | 12.0674(11)   | 12.1603(15)  |
| <i>c</i> [Å]                                | 7.5123(7)   | 26.820(3)   | 12.955(7)   | 12.7544(11)   | 12.8887(16)  |
| $\alpha$ [°]                                | 90  | 90  | 71.269(13)  | 72.987(2)   | 72.482(2)  |
| $\beta$ [°]                                 | 90  | 97.961(2)   | 86.197(18)  | 85.737(2)   | 85.863(2)  |
| $\gamma$ [°]                                | 90  | 90  | 82.699(14)  | 83.075(2)   | 83.337(2)  |
| <i>V</i> [Å <sup>3</sup> ]                  | 1525.4(2)   | 1591.9(3)   | 1529.0(15)  | 1515.4(2)   | 1556.7(3)  |
| <i>Z</i>                                    | 4   | 4   | 4   | 4   | 4  |
| $\lambda$ [Å]                               | 0.71073   | 0.71073   | 0.71073   | 0.71073   | 0.71073  |
| $\rho_{\text{calcd}}$ [g cm <sup>-3</sup> ] | 1.555   | 2.059   | 1.959   | 2.185   | 2.506  |
| <i>F</i> [000]                              | 736   | 936   | 880   | 952   | 1080   |
| $\mu$ [mm <sup>-1</sup> ]                   | 1.538   | 9.070   | 6.023   | 6.021   | 13.684   |
| $\theta$ [°]                                | 2.86–24.96  | 2.57–24.97  | 2.51–23.95  | 2.54–25.04  | 2.61–31.94   |
| Index ranges                                | –10 ≤ <i>h</i> ≤ 10<br>–26 ≤ <i>k</i> ≤ 26<br>–8 ≤ <i>l</i> ≤ 8 | –8 ≤ <i>h</i> ≤ 9<br>–5 ≤ <i>k</i> ≤ 9<br>–31 ≤ <i>l</i> ≤ 31   | –11 ≤ <i>h</i> ≤ 12<br>–14 ≤ <i>k</i> ≤ 14<br>–15 ≤ <i>l</i> ≤ 14 | –12 ≤ <i>h</i> ≤ 12<br>–14 ≤ <i>k</i> ≤ 14<br>–15 ≤ <i>l</i> ≤ 13 | –7 ≤ <i>h</i> ≤ 13<br>–15 ≤ <i>k</i> ≤ 15<br>–16 ≤ <i>l</i> ≤ 16 |
| <i>T</i> [K]                                | 100(2)  | 298(2)  | 298(2)  | 298(2)  | 298(2)   |
| <i>R</i> <sub>1</sub>                       | 0.0215  | 0.0644  | 0.0438  | 0.0166  | 0.0320   |
| <i>wR</i> <sub>2</sub>                      | 0.0481  | 0.1849  | 0.1065  | 0.0394  | 0.0820   |
| <i>R</i> <sub>merge</sub>                   | 0.0257  | 0.0751  | 0.0731  | 0.0183  | 0.0410   |
| Parameters                                  | 190   | 160   | 331   | 379   | 379  |
| GOF   | 1.024   | 1.085   | 1.025   | 1.050   | 1.185  |
| Total reflns                                | 11 553  | 11 915  | 21 036  | 29 289  | 24 568   |
| Unique reflns                               | 2681  | 2806  | 5597  | 5407  | 6805   |
| Obsd reflns                                 | 2445  | 2295  | 3920  | 5049  | 5752   |
| CCDC no.                                    | 946622  | 946625  | 946624  | 946623  | 946626   |

various diamines. It is the first report on the synthesis of neutral thiasalen complexes of Pd and Pt and selenosalen complexes of Ni, Pd and Pt.

## Experimental section

All reagents were purchased from Aldrich/Merck and used without further purification. Acetonitrile was distilled from P<sub>2</sub>O<sub>5</sub> and kept over molecular sieves. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded either on Bruker 500 MHz or on JEOL-FT NMR-AL 400 MHz spectrometer using DMSO-*d*<sub>6</sub> as solvent and tetramethylsilane (SiMe<sub>4</sub>) as internal standards. <sup>77</sup>Se NMR spectra were recorded on Bruker 500 MHz spectrometer using DMSO-*d*<sub>6</sub> as solvent. <sup>77</sup>Se NMR chemical shifts are reported using Ph<sub>2</sub>Se<sub>2</sub> as external standard with chemical shifts of 470 ppm with respect to Me<sub>2</sub>Se, thus the values are reported with respect to Me<sub>2</sub>Se. IR spectra of the compounds have been recorded on a Perkin-Elmer spectrophotometer as KBr pellets. The mass spectra were recorded on a MICROMAX Q-TOF-MICRO instrument. Melting points were measured using a digital melting point apparatus, SECOR INDIA.

### Crystal structure determination

Single crystals of the compounds suitable for X-ray diffraction were grown from dimethyl formamide/dimethyl sulfoxide solution by diffusing diethyl ether vapors in a closed beaker. The crystals were carefully chosen using a stereomicroscope supported by a rotatable polarizing stage. The data were collected on Bruker's KAPPA APEX II CCD Duo with graphite monochromated Mo-K $\alpha$  radiation (0.71073 Å). The crystals were glued to

a thin glass fibre using FOMBLIN immersion oil and mounted on the diffractometer. The intensity data were processed using Bruker's suite of data processing programs (SAINT), and absorption corrections were applied using SADABS.<sup>24</sup> The crystal structure was solved by direct methods using SHELXS-97 and the data were refined by full matrix least-squares refinement on *F*<sup>2</sup> with anisotropic displacement parameters for non-H atoms, using SHELXL-97.<sup>25</sup> ORTEP diagrams are drawn from X-seed version 2.0.<sup>26</sup>

### Thiasalen Ni(II) complex 14

To a solution of bis(*o*-formylphenyl)disulfide **12** (74 mg, 0.27 mmol) in 10 mL dry methanol, [Ni(COD)<sub>2</sub>] (74 mg, 0.27 mmol) and ethylenediamine (16 mg, 0.27 mmol) were added at room temperature under nitrogen atmosphere. The reaction mixture was stirred for 5 days. Precipitate was filtered, washed thoroughly with methanol and dried in vacuum (yield: 72 mg, 75%). Mp 272 °C (d). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.59 (s, 2H); 7.49 (m, 4H); 7.22 (m, 2H); 7.03 (m, 2H), 3.72 (s, 4H) ppm. <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  163.77, 144.70, 134.96, 130.41, 129.69, 129.36, 121.65, 61.26 ppm. IR  $\nu_{\text{max}}$  (KBr, cm<sup>-1</sup>): 1610 (C=N). Anal. Calcd (%) for C<sub>16</sub>H<sub>14</sub>N<sub>2</sub> Ni S<sub>2</sub>: C, 53.81; H, 3.95; N, 7.84. Found: C, 54.65; H, 4.02; N, 7.91%. ESI-MS calcd for {(C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>NiS<sub>2</sub> + H)<sup>+</sup>}, 357.0030, found, 356.3700.

### Thiasalen Pd(II) complex 15

To a solution of bis(*o*-formylphenyl)disulfide **12** (100 mg, 0.36 mmol) in 10 mL dry acetonitrile, [Pd(PPh<sub>3</sub>)<sub>4</sub>] (410 mg, 0.36 mmol) and ethylenediamine (26 mg, 0.44 mmol) were



added at room temperature under nitrogen atmosphere. The reaction mixture was stirred for 5 days. Precipitate was filtered, washed thoroughly with acetonitrile and dried in vacuum (yield: 117 mg, 76%). Mp 290 °C (d).  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  8.72 (1H), 7.61–7.06 (4H, Ar-H), 3.99 (s, 2H) ppm.  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  161.80, 144.06, 136.93, 131.82, 130.87, 130.62, 121.91, 61.76 ppm. IR  $\nu_{\text{max}}$  (KBr,  $\text{cm}^{-1}$ ): 1626 (C=N). Anal. Calcd (%) for  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{PdS}_2$ : C, 47.47; H, 3.49; N, 6.92. Found: C, 47.03; H, 3.29; N, 6.63%.

#### Thiasalen Pt(II) complex 16

To a solution of bis(*o*-formylphenyl)disulfide **12** (100 mg, 0.36 mmol) in 10 mL dry acetonitrile,  $[\text{Pt}(\text{PPh}_3)_4]$  (450 mg, 0.36 mmol) and ethylenediamine (26 mg, 0.44 mmol) were added at room temperature under nitrogen atmosphere. The reaction mixture was stirred for 5 days. Precipitate was filtered, washed thoroughly with acetonitrile and dried in vacuum (yield: 92 mg, 51%). Mp 285 °C (d).  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  9.02 (1H), 7.67–7.04 (4H, Ar-H), 3.94 (s, 2H) ppm.  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  157.20, 139.84, 135.89, 131.95, 131.08, 130.63, 122.03, 62.76 ppm. IR  $\nu_{\text{max}}$  (KBr,  $\text{cm}^{-1}$ ): 1617 (C=N). Anal. Calcd (%) for  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{PtS}_2$ : C, 38.94; H, 2.86; N, 5.68. Found: C, 38.76; H, 2.74; N, 5.31%.

#### Selenasalen Ni(II) complex 17

To a solution of bis(*o*-formylphenyl) diselenide **13** (100 mg, 0.27 mmol) in 10 mL dry methanol,  $[\text{Ni}(\text{COD})_2]$  (74 mg, 0.27 mmol) and ethylene diamine (17 mg, 0.27 mmol) were added at room temperature under nitrogen atmosphere. The reaction mixture was stirred for 5 days. Precipitate was filtered, washed thoroughly with methanol and dried in vacuum (yield: 78 mg, 61%). Mp 285 °C (d).  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ ):  $\delta$  8.66 (s, 1H); 7.68 (m, 2H), 7.56 (m, 2H), 7.19 (m, 4H), 3.74 (s, 4H) ppm.  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ ):  $\delta$  164.76, 136.40, 136.00, 132.72, 131.78, 130.22, 123.45, 62.04 ppm.  $^{77}\text{Se}$  NMR (95 MHz, DMSO- $d_6$ ):  $\delta$  354.9 ppm. IR  $\nu_{\text{max}}$  (KBr,  $\text{cm}^{-1}$ ): 1609 (C=N). Anal. Calcd (%) for  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{Se}_2\text{Ni}$ : C, 42.62; H, 3.13; N, 6.21. Found: C, 41.98; H, 2.95; N, 6.41%. ESI-MS calcd for  $\{(\text{C}_{16}\text{H}_{14}\text{N}_2\text{NiSe}_2 + \text{H})^+\}$ , 452.8919, found, 452.1934.

#### Selenasalen Pd(II) complex 18

To a solution of bis(*o*-formylphenyl) diselenide **13** (100 mg, 0.27 mmol) in 10 mL dry methanol,  $[\text{Pd}(\text{PPh}_3)_4]$  (310 mg, 0.27 mmol) and ethylenediamine (16 mg, 0.27 mmol) were added at room temperature under nitrogen atmosphere. The reaction mixture was stirred for 5 days. Precipitate was filtered, washed thoroughly with methanol and dried in vacuum (yield: 81 mg, 60%). Mp 283 °C (d).  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  8.76 (1H), 7.80–7.18 (4H, Ar-H), 3.97 (s, 2H) ppm.  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ ):  $\delta$  162.69, 137.70, 134.70, 133.66, 132.84, 131.46, 123.39, 62.45 ppm.  $^{77}\text{Se}$  NMR (95 MHz, DMSO- $d_6$ ):  $\delta$  393.7 ppm. IR  $\nu_{\text{max}}$  (KBr,  $\text{cm}^{-1}$ ): 1622 (C=N). Anal. Calcd (%) for  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{PdSe}_2$ : C, 38.54; H, 2.83; N, 5.62. Found: C, 40.79; H, 2.74; N, 5.67%.

#### Selenasalen Pt(II) complex 19

To a solution of bis(*o*-formylphenyl)diselenide **13** (100 mg, 0.27 mmol) in 10 mL dry methanol,  $[\text{Pt}(\text{PPh}_3)_4]$  (340 mg, 0.27 mmol) and ethylenediamine (16 g, 0.27 mmol) were added at room temperature under nitrogen atmosphere. The reaction mixture was stirred for 5 days. Precipitate was filtered, washed thoroughly with methanol and dried in vacuum (yield: 96 mg, 60%). Mp 297 °C (d).  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ ):  $\delta$  9.09 (1H), 7.80–7.16 (4H, Ar-H), 3.91 (s, 2H) ppm.  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ ):  $\delta$  158.26, 137.01, 134.59, 132.71, 131.06, 123.67, 63.77 ppm.  $^{77}\text{Se}$  NMR (95 MHz, DMSO- $d_6$ ):  $\delta$  318.9 ppm. IR  $\nu_{\text{max}}$  (KBr,  $\text{cm}^{-1}$ ): 1611 (C=N). Anal. Calcd (%) for  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{PtSe}_2$ : C, 32.72; H, 2.40; N, 4.77. Found: C, 33.98; H, 2.26; N, 5.05%.

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