

# Nickel-Selenium & Palladium-Selenium complexes

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# INTRODUCTION

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- There is a growing interest in metal complexes with selenium ligands
  - Literature on nickel complexes with selenium ligands – scanty
- Hence, the aim of this research project is to report new nickel-selenium complexes and add to the existing knowledge of nickel complexes with selenium ligands.

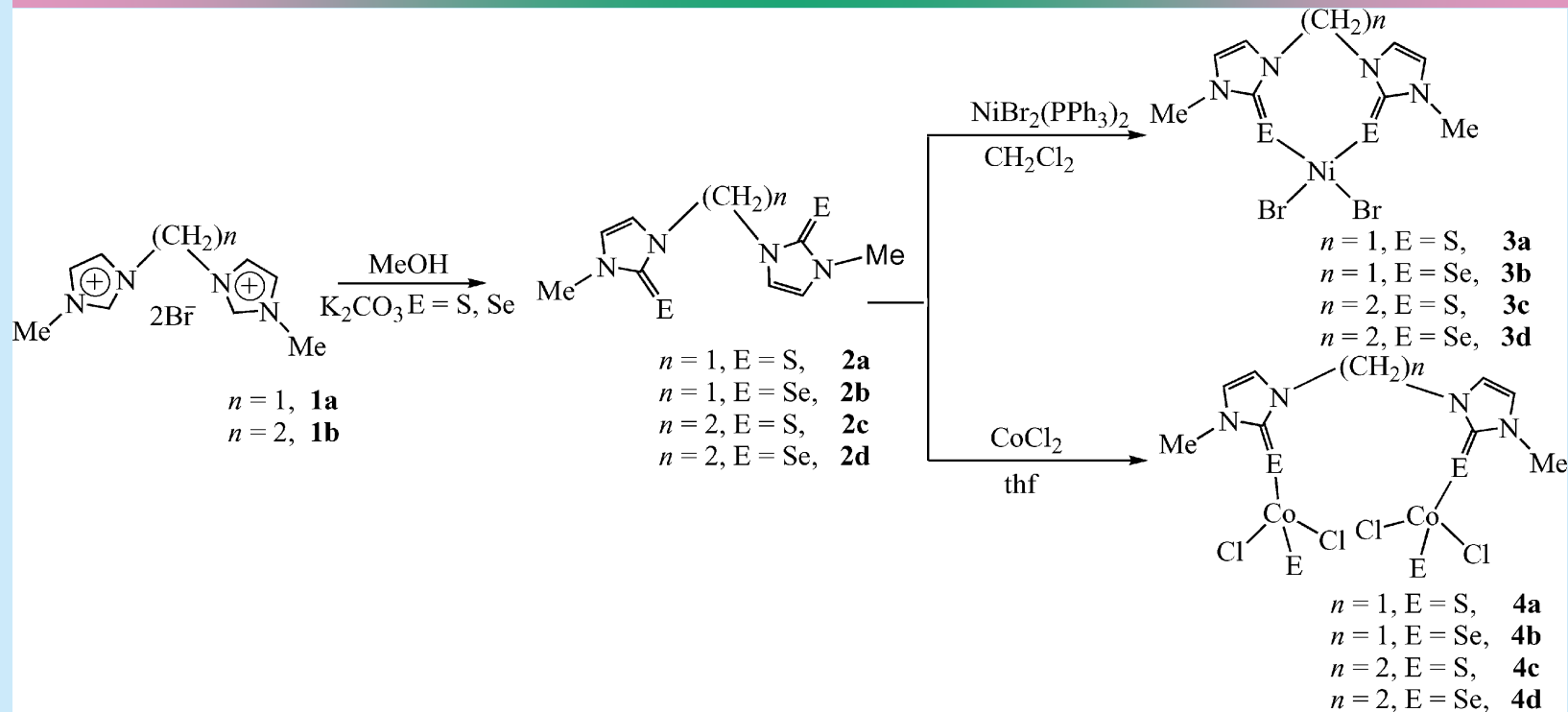


# FINDINGS



# **Nickel-selenium complexes**

**Jia, W.-G.; Huang, Y.-B.; Lin, Y.-J.; Wang, G.-L.; Jin, G.-X. Nickel Complexes and Cobalt Coordination Polymers with Organochalcogen (S, Se) Ligands Bearing an N-Methylimidazole Moiety: Syntheses, Structures, and Properties. *Eur. J. Inorg. Chem.* 2008, 4063-4073.**



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- A series of mononuclear Ni complexes **3a–d** with eight or nine-membered rings were obtained by the reaction of  $\text{NiBr}_2(\text{PPh}_3)_2$  and organochalcogen (S, Se) ligands bearing N-methylimidazole, mbit (**2a**), mbis (**2b**), ebit (**2c**), and ebis (**2d**).
- [mbit = 1,1'-methylenebis(1,3-dihydro-3-methyl-2H-imidazole-2-thione), mbis = 1,1'-methylene-bis(1,3-dihydro-3-methyl-2H-imidazole-2-selone), ebit = 1,1'-(1,2-ethanediyl)bis(1,3-dihydro-3-methyl-1H-imidazole-2-thione), ebis = 1,1'-(1,2-ethanediyl)bis(1,3-dihydro-3-methyl-1H-imidazole-2-selone)]

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- Dichloromethane solutions of equimolar amounts of  $\text{Ni}(\text{PPh}_3)\text{Br}_2$  and each of the ligands **2a–d** were stirred at room temperature under an atmosphere of nitrogen for 10 h to produce compounds **3a–d** in yields of 75, 40, 60, and 32%, respectively (Figure 1). The compounds with sulfur ligands are stable to air and moisture, whereas those with selenium ligands are very sensitive to air and moisture. All the nickel complexes are moderately soluble in polar solvent such as MeCN, DMSO, and DMF, but insoluble in common organic solvents such as  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , thf, and toluene.
- The NMR spectra of four nickel complexes are not informative because of the interfering effect caused by their paramagnetism. This phenomenon can be seen from other tetrahedral nickel complexes.

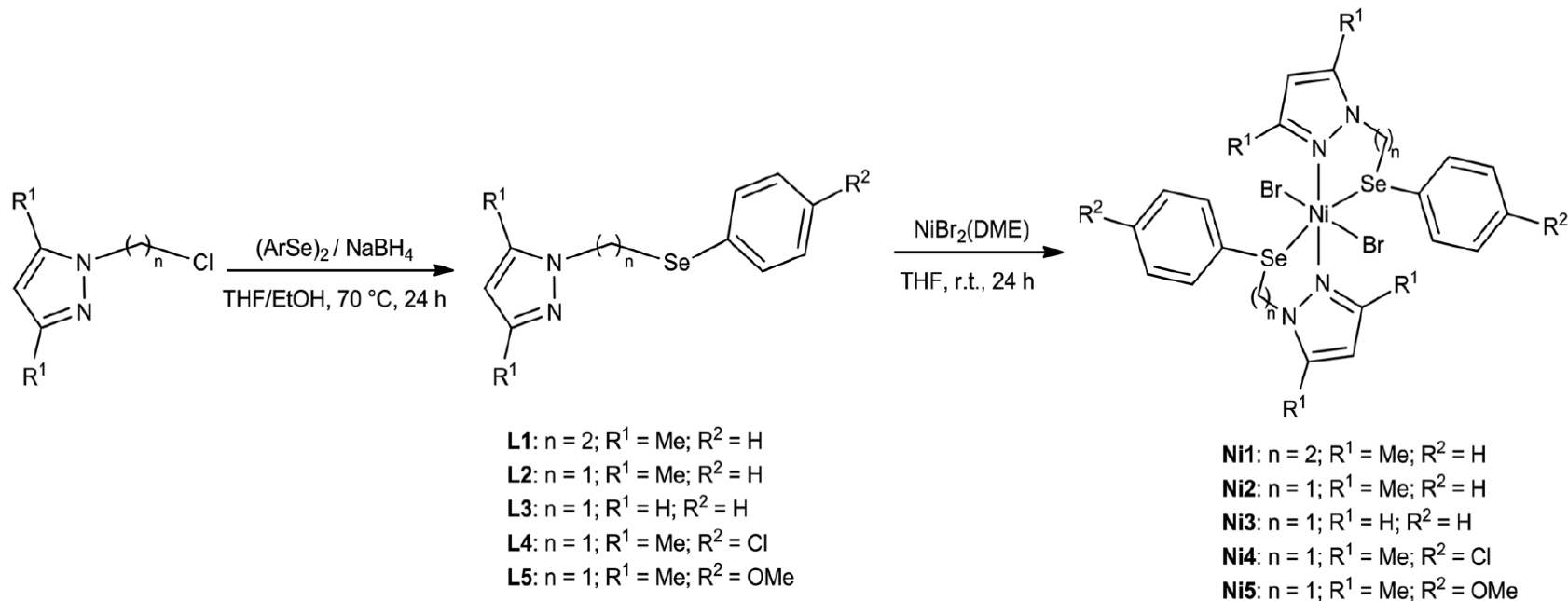
**Jia, W.-G.; Huang, Y.-B.; Lin, Y.-J.; Wang, G.-L.; Jin, G.-X. Nickel Complexes and Cobalt Coordination Polymers with Organochalcogen (S, Se) Ligands Bearing an N-Methylimidazole Moiety: Syntheses, Structures, and Properties. *Eur. J. Inorg. Chem.* 2008, 4063-4073.**

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- In comparison to the IR spectra of the corresponding free ligands, all the Ni(II) complexes have slight changes. The IR bands that should be of most interest in investigating the coordination mode of the ligand are  $\nu(\text{NCN})$  and  $\nu(\text{C}=\text{S})$  or  $\nu(\text{C}=\text{Se})$ . The IR spectrum of 3a in the solid state exhibited intense N–C–N and C=S stretching at about 1570, 1195, and 1153  $\text{cm}^{-1}$ . The IR spectra of complex 3b in the solid state exhibited intense N–C–N and C=Se stretching at about 1570, 1194, and 1133  $\text{cm}^{-1}$ , which is in agreement with the data of the structures.
- Bands at around 1565, 1193, and 1146  $\text{cm}^{-1}$  in the IR spectra can be assigned to the N–C–N and C=S stretching for 3c. The IR spectra of 3d show the N–C–N and C=Se stretching at around 1566, 1177, and 1126  $\text{cm}^{-1}$ .



**Dresch L. C.; de Araujo B. B.; de L. Casagrande, Jr. O.; Stieler R. A novel class of nickel (II) complexes containing selenium-based bidentate ligands applied in ethylene oligomerization. *RSC Advances* 2016, 6, 104338-104344.**



**Scheme 1** Synthesis of arylselenenyl-pyrazolyl ligands (L1–L5) and  $[\text{NiBr}_2(\text{N}^{\text{A}}\text{Se})_2]$  complexes (Ni1–Ni5).

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- $\text{NiBr}_2\{\text{bis}(3,5\text{-dimethyl-1-(2-(phenylselenenyl)ethyl)-1H-pyrazole})\}$  (Ni1). To a solution of  $\text{NiBr}_2(\text{DME})$  (0.165 g, 0.53 mmol) in THF (15 mL) was added a solution of L1 (0.310 g, 1.11 mmol) in THF (5 mL). The reaction mixture was stirred for 24 h at room temperature. Then, the solvent was removed under vacuum resulting in a purple solid residue that was washed with  $\text{Et}_2\text{O}$  (3 x 10 mL). Complex Ni1 was obtained as a purple solid (0.199 g, 48%). IR (ATR,  $\text{cm}^{-1}$ ): 3051 (m), 2922 (m), 2860 (m), 1720 (w), 1577 (m), 1551 (s), 1465 (s), 1435 (s), 1384 (s), 1301 (m), 1253 (m), 1197 (w), 1152 (m), 1020 (m), 852 (w), 794 (m), 734 (s), 689 (m), 668 (m), 614 (w). Anal. calc. for  $\text{C}_{26}\text{H}_{32}\text{Br}_2\text{N}_4\text{NiSe}_2$ : C, 40.19; H, 4.15; N, 7.21. Found: C, 39.07; H, 4.07; N, 6.54. ESI-HRMS ( $\text{CH}_3\text{OH}$ ,  $m/z$ ): 696.9516  $[\text{M} - \text{Br}]^+$  (calc. for  $\text{C}_{26}\text{H}_{32}\text{Br}_2\text{N}_4\text{NiSe}_2$ : 696.9494).

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- $\text{NiBr}_2\{\text{bis}(3,5\text{-dimethyl-1-}((\text{phenylselenyl})\text{methyl})\text{-1H-pyrazole})\}$  (Ni2). (0.156 g, 74%). IR (ATR,  $\text{cm}^{-1}$ ): 3053 (w), 2922 (m), 2863 (m), 1715 (w), 1661 (w), 1552 (m), 1460 (m), 1415 (s), 1378 (m), 1285 (w), 1235 (m), 1041 (m), 998 (m), 794 (m), 738 (s), 665 (m), 661 (m), 609 (w). Anal. calc. for  $\text{C}_{24}\text{H}_{28}\text{Br}_2\text{N}_4\text{Ni Se}_2$ : C, 38.49; H, 3.77; N, 7.48. Found: C, 38.66; H, 4.01; N, 7.19. ESI-HRMS ( $\text{CH}_3\text{OH}$ ,  $m/z$ ): 668.9186  $[\text{M} - \text{Br}]^+$  (calc. for  $\text{C}_{24}\text{H}_{28}\text{Br}_2\text{N}_4\text{Ni Se}_2$ : 668.9181).
- $\text{NiBr}_2\{\text{bis}(1-((\text{phenylselenyl})\text{methyl})\text{-1H-pyrazole})\}$  (Ni3). (0.177 g, 81%). IR (ATR,  $\text{cm}^{-1}$ ): 3047 (w), 2938 (w), 2854 (w), 1574 (w), 1479 (m), 1430 (m), 1333 (w), 1241 (m), 1154 (m), 1055 (m), 987 (m), 902 (m), 772 (m), 732 (s), 685 (m), 661 (m), 597 (m). Anal. calc. for  $\text{C}_{20}\text{H}_{20}\text{Br}_2\text{N}_4\text{NiSe}_2$ : C, 34.67; H, 2.91; N, 8.09. Found: C, 34.70; H, 3.65; N, 7.08. ESI-HRMS ( $\text{CH}_3\text{OH}$ ,  $m/z$ ): 612.8555  $[\text{M} - \text{Br}]^+$  (calc. for  $\text{C}_{20}\text{H}_{20}\text{Br}_2\text{N}_4\text{NiSe}_2$ : 612.8555).

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- $\text{NiBr}_2\{\text{bis}(1-(((4\text{-chlorophenyl})\text{selenyl})\text{methyl})\text{-}3,5\text{-dimethyl-}1\text{H-pyrazole})\}$  (Ni4). (0.165 g, 0.55 mmol) in THF (5 mL) to give Ni4 as a dark green solid. (0.135 g, 66%). IR (ATR,  $\text{cm}^{-1}$ ):  $\nu$  3050 (m), 2921 (m), 2856 (m), 2364 (w), 1554 (m), 1467 (m), 1416 (m), 1381 (m), 1285 (w), 1235 (m), 1088 (s), 1042 (m), 1005 (m), 806 (s), 726 (m), 663 (s), 612 (m). Anal. calc. for  $\text{C}_{24}\text{H}_{26}\text{Br}_2\text{Cl}_2\text{N}_4\text{NiSe}_2$ : C, 35.25; H, 3.20; N, 6.85. Found: C, 34.76; H, 3.80; N, 5.91. ESI-HRMS ( $\text{CH}_3\text{OH}$ ,  $m/z$ ): 738.8393 [ $\text{M} - \text{Br}$ ]<sup>+</sup> (calc. for  $\text{C}_{24}\text{H}_{26}\text{Br}_2\text{Cl}_2\text{N}_4\text{NiSe}_2$ : 738.8381).
- $\text{NiBr}_2\{\text{bis}(1-(((4\text{-methoxyphenyl})\text{selenyl})\text{methyl})\text{-}3,5\text{-dimethyl-}1\text{H-pyrazole})\}$  (Ni5). (0.165 g, 0.56 mmol) in THF (5 mL) to give Ni5 as a dark green solid. (0.149 g, 73%). IR (ATR,  $\text{cm}^{-1}$ ): 3051 (m), 2916 (m), 2836 (m), 1717 (w), 1625 (w), 1585 (m), 1554 (m), 1489 (s), 1458 (m), 1416 (m), 1384 (m), 1287 (m), 1247 (s), 1175 (m), 1104 (w), 1020 (m), 809 (m), 657 (w), 597 (w), 518 (w). Anal. calc. for  $\text{C}_{26}\text{H}_{32}\text{Br}_2\text{N}_4\text{NiO}_2\text{Se}_2$ : C, 38.60; H, 3.99; N, 6.93. Found: C, 37.83; H, 3.94; N, 5.67. ESI-HRMS ( $\text{CH}_3\text{OH}$ ,  $m/z$ ): 728.9393 [ $\text{M Br}$ ]<sup>+</sup> (calc. for  $\text{C}_{26}\text{H}_{32}\text{Br}_2\text{N}_4\text{NiO}_2\text{Se}_2$ : 728.9323).

Brennan, J. G.; Slegrist, T.; Kwon, Y. U.; Stuczynski S. M.; Steigerwald M. L.  $\text{Ni}_{23}\text{Se}_{12}(\text{PEt}_3)_{13}$ . An Intramolecular Intergrowth of NiSe and Ni. *J. Am. Chem. Soc.* 1992, 114, 10334-10338.

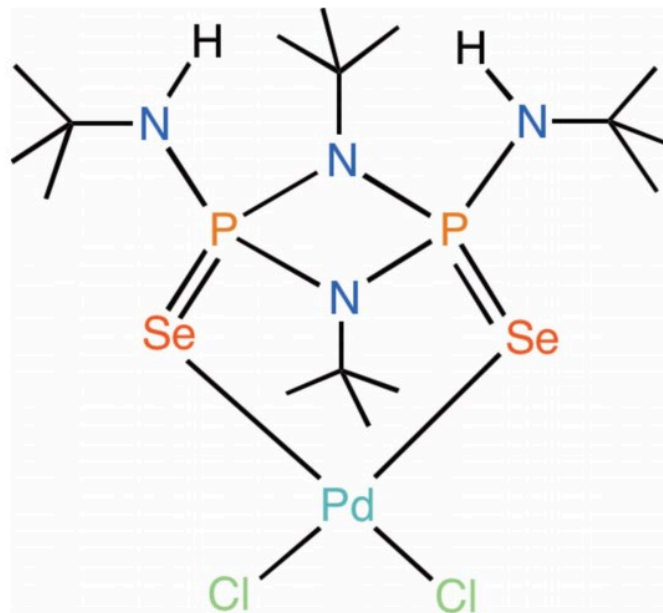
- $\text{Ni}(\text{COD})_2$  (2.46 g, 9.0 mmol) was suspended in toluene (50 mL) to which  $\text{PEt}_3$  (0.2 mL, 1.7 mmol) had been added. In a separate vessel  $\text{Et}_3\text{PSe}$  (6.71 g, 34.1 mmol) was dissolved in toluene (100 mL). The solution of  $\text{Et}_3\text{PSe}$  was diluted with heptane (100 mL), taking care that the phosphine selenide remained in solution. The  $\text{Ni}(\text{COD})_2$  suspension was added to the  $\text{Et}_3\text{PSe}$  solution via pipette, and the mixture was stirred at room temperature overnight after which point the mixture was filtered. This solution deposited crystalline solid over the space of 2 weeks at room temperature. The supernatant liquor was removed, and the solid was washed with pentane to give the dark, crystalline product (0.22 g, 15%). Elemental Anal. Found (calculated for  $\text{Ni}_{23}\text{Se}_{12}\text{P}_{13}\text{C}_{78}\text{H}_{195}$ ): C, 24.16 (24.44); H, 4.95 (5.13); Ni, 34.95 (35.22); P, 10.26 (10.50); Se, 24.80 (24.70).



# **Palladium-selenium complexes**

Bonnette, A.; Mague, J. T.; Chandrasekaran P. Crystal structure of a palladium(II) complex containing the wide bite-angle bis(selenium) ligand, cis-[(*t* BuNH)(Se)P(I-Nt Bu)<sub>2</sub>P(Se)(NHt Bu)]. *Acta Cryst.* **2018**, **E74**, 180-183.

- A dichloromethane solution (10 mL) of [Pd(COD)Cl<sub>2</sub>] (100 mg, 0.35 mmol) was added dropwise to a solution of cis-[(*t* BuHN)(Se)P(BuN)<sub>2</sub>P(Se)(NH<sup>*t*</sup> Bu)] (175 mg, 0.35 mmol) in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> under an N<sub>2</sub> atmosphere at ambient temperature. The resultant dark-orange solution was stirred for 6 h. The solution was then concentrated to 10 mL, diluted with 10 mL of pentane, and stored at 248 K for a day to afford the analytically pure orange crystalline product. X-ray quality crystals were obtained by slow evaporation from a DMF solution at room temperature.
- Yield: 76% (206 mg, 0.067 mmol), m.p. 455–457 K.



Bonnette, A.; Mague, J. T.; Chandrasekaran P. Crystal structure of a palladium(II) complex containing the wide bite-angle bis(selenium) ligand, cis-[(t BuNH)(Se)P(I-Nt Bu)2P(Se)(NHt Bu)]. *Acta Cryst.* **2018**, **E74**, **180-183**.

- <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): 1.44 (s, 18H, tBu), 1.57 (s, 18H, tBu), 2.3 (br s, 2H, NH). IR (cm<sup>-1</sup>): 3175 (br w), 2974 (w), 1469 (w), 1392 (w), 1367 (m), 1367 (m), 1227 (m), 1184 (s), 1028 (s), 893 (s), 837 (w), 733 (m), 683 (m). Absorption spectrum [CH<sub>2</sub>Cl<sub>2</sub>; max, nm (εM, M<sup>-1</sup> cm<sup>-1</sup>)]: 247 (12068), 294 (15752), 355 (6827). Analysis calculated for C<sub>16</sub>H<sub>38</sub>N<sub>4</sub>P<sub>2</sub>Se<sub>2</sub>PdCl<sub>2</sub>: C, 28.11; H, 5.60; N, 8.19. Found: C, 28.37; H, 6.01; N, 28.74.



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- Ferdinand