

*Dedicated to Academician Cristian Silvestru  
on the occasion of his 70<sup>th</sup> anniversary*

## SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF SILVER(I) AND GOLD(I) METAL COMPLEXES CONTAINING A NEW HOMOLEPTIC DIORGANOSELENIUM(II) LIGAND

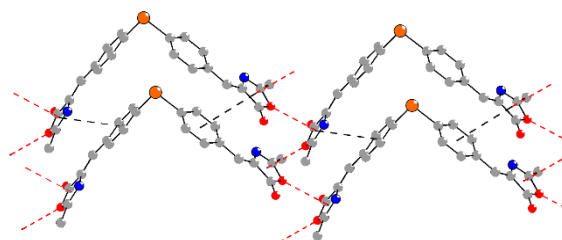
Andrei-Dănuț DĂNILĂ,<sup>a</sup> Cosmina BOHAN,<sup>a</sup> Nora CHIOREAN,<sup>a</sup> Emese GAL<sup>b</sup> and Alexandra POP<sup>a\*</sup>

<sup>a</sup>Supramolecular Organic and Organometallic Chemistry Centre, Chemistry Department, Faculty of Chemistry and Chemical Engineering, “Babeș-Bolyai” University, RO-400028 Cluj-Napoca, Roumania

<sup>b</sup>Research Center on Fundamental and Applied Heterochemistry, Faculty of Chemistry and Chemical Engineering, “Babeș-Bolyai” University, Str. Arany Janos 11, RO-400028 Cluj-Napoca, Roumania

Received June 18, 2025

The homoleptic diorganoselenide(II) [(*Z*)-4'-{2-CH<sub>3</sub>-(4*H*)-oxazol-5-one}CHC<sub>6</sub>H<sub>4</sub>]<sub>2</sub>Se (**1**), and its metal complexes [Ag{(Z)-4'-{2-CH<sub>3</sub>-(4*H*)-oxazol-5-one}CHC<sub>6</sub>H<sub>4</sub>]<sub>2</sub>Se][OTf] (**2**), [Ag{(Z)-4'-{2-CH<sub>3</sub>-(4*H*)-oxazol-5-one}CHC<sub>6</sub>H<sub>4</sub>]<sub>2</sub>Se][PF<sub>6</sub>] (**3**) and [AuCl{(Z)-4'-{2-CH<sub>3</sub>-(4*H*)-oxazol-5-one}CHC<sub>6</sub>H<sub>4</sub>]<sub>2</sub>Se] (**4**), were prepared and characterized in solution and in solid state by multinuclear NMR spectroscopy, mass spectrometry, molar conductivities, FT-IR spectroscopy. For compound **1**, the molecular structure was determined by single crystal X-ray diffraction. In the crystal of **1**, a supramolecular network formed by  $\pi$  interactions, was observed. UV-Vis measurements revealed a hypsochromic shift, with higher intensity of the bands in the spectra of the metal complexes **2** – **4**, relative to compound **1**.



### INTRODUCTION

Homoleptic diorganoselenides(II) are undoubtedly an important class of organoselenium derivatives, due to their uses in several applicative research fields.<sup>1,2</sup> Starting with their use in coordination chemistry as ligands to stabilize transition metal complexes,<sup>3–5</sup> to their antioxidant activity,<sup>6</sup> such diorganoselenides(II) are a continuous source of interest in the scientific community. Moreover, introducing selenium into the skeleton of some organic compounds might be a

useful tool for the adjustment of the biological activity, *e.g.* diorganoselenides containing substituted thiazoles, thiazolidinones, azetidinones, triazolines, and glycols fragments were prepared and evaluated as antibacterial agents.<sup>7</sup> One of the most important steps in the development of new compounds targeted for different applications is the controlling of the coordination behaviour of the ligands, *e.g.* MOFs with different dimensionality having luminescent properties were prepared using 1,5-bis(3,5-dimethylpyrazol-1-yl)-3-selenapentane and Ag(I) building blocks.<sup>8</sup> Luminescent materials

\* Corresponding author: alexandra.m.pop@ubbcluj.ro

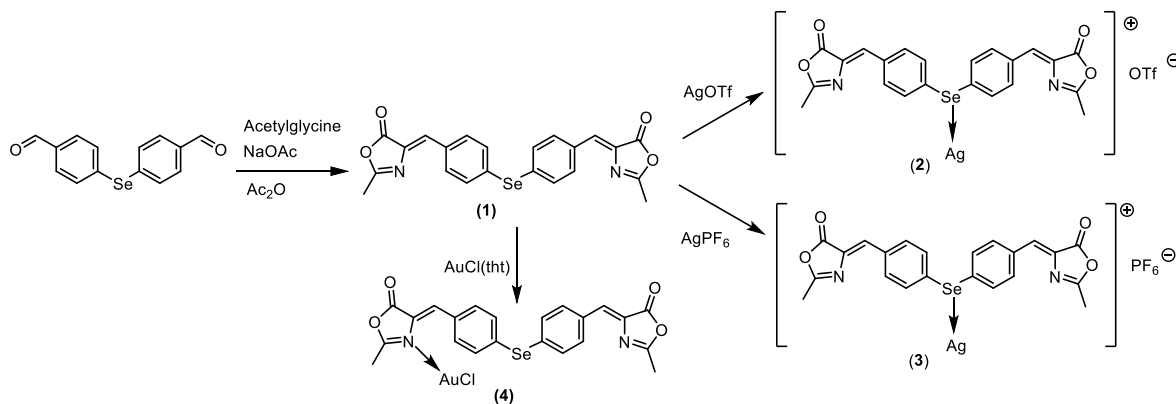
garnered significant attention for their potential applications in optoelectronics. To tune the known optical properties of the oxazolone derivatives,<sup>9–12</sup> several organoselenides containing oxazolone into their skeleton were already reported in our group (*i.e.* (*n*-Bu)[(*Z*)-4'-{2-C<sub>6</sub>H<sub>5</sub>-(4*H*)-oxazol-5-one}CHC<sub>6</sub>H<sub>4</sub>]Se,<sup>13</sup> and [(*Z*)-2'-{2-C<sub>6</sub>H<sub>5</sub>-(4*H*)-oxazol-5-one}CHC<sub>6</sub>H<sub>4</sub>]<sub>2</sub>Se)<sup>14</sup> and their coordination behaviour was investigated with several late *d* transition metals.

Combining this background with our interest in the preparation of silver and gold complexes containing organoselenium derivatives,<sup>15–17</sup> we report herein our latest results regarding synthesis, characterization and investigation of the reactivity by complexation reactions with AgOTf, AgPF<sub>6</sub> and AuCl(tht) of a new homoleptic derivative, [(*Z*)-4'-{2-CH<sub>3</sub>-(4*H*)-oxazol-5-one}CHC<sub>6</sub>H<sub>4</sub>]<sub>2</sub>Se (**1**).

## RESULTS AND DISCUSSION

### Synthesis

For the preparation of the target homoleptic diorganoselenide(II), the [4-(O=CH)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>Se<sup>14</sup> was



Scheme 1 – Synthesis of compound **1** and metal complexes **2–4**.

### Solutions behaviour

The proposed structure for compound **1** was confirmed by multinuclear NMR spectra. The presence of only one set of resonance signals both in <sup>1</sup>H NMR and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of compound **1** and complexes **2–4**, respectively suggested the equivalence of the organic groups attached to the selenium atom. The <sup>1</sup>H NMR spectrum of **1** revealed four resonance signals, two doublets for the aromatic rings attached to the selenium atom ( $\delta = 7.98$  ppm and 7.51 ppm, respectively), one singlet around  $\delta$  7.0 ppm corresponding to the vinylic

prepared following the previously reported method and was reacted following the Erlenmeyer-Plöchl procedure,<sup>18</sup> with *N*-acetyl glycine and sodium acetate (1:2:4 molar ratio) in acetic anhydride. The reaction mixture was refluxed for 4 hours at 100°C, and after cooling the solution at room temperature, the desired derivative **1** was precipitated and washed several times with cold EtOH (Scheme 1). As observed previously and reported also in the literature, only the *Z* isomer was isolated.<sup>19</sup> Diorganoselenide **1** was isolated as orange solid and was further reacted in 1 : 1 molar ratio with AgOTf and AgPF<sub>6</sub> in acetone (in the absence of light) and in CHCl<sub>3</sub> with AuCl(tht). Complexes **2–4** (Scheme 1) were isolated as intense orange to red solids, in very good yields (94–95%).

All the compounds, **1–4** were characterized both in solution by multinuclear NMR spectroscopy, molar conductivities and mass spectrometry, and in the solid state by IR spectroscopy. The molecular structure of **1** was determined by single crystal X-Ray diffraction. UV-Vis measurements were used for the investigation of the optical properties of the compounds. Based on the mentioned analyses, the proposed structures for the metal complexes **2–4**, in solution, are depicted in Scheme 1.

fragment and one singlet at  $\delta$  2.4 ppm for the methyl fragments attached to the oxazolone rings. Same pattern of the signals was observed for the metal complexes, with the signals slightly shifted when comparing with the proligand **1**. The same behaviour was observed also in the <sup>13</sup>C{<sup>1</sup>H} NMR spectra, all the compounds exhibited the same pattern, with singlet resonance signals, slightly shifted in the metal complexes.

One singlet resonance signal was observed in the <sup>77</sup>Se{<sup>1</sup>H} NMR spectra at 436 ppm for **1** and complex **4**, at 409 ppm for **2** and 393 ppm for **3**, respectively. The same chemical shift for proligand **1** and gold

complex **4** suggested that the gold atom in complexes **4** is not interacting with the selenium atom in solution, probably only with the nitrogen atoms in the oxazolone rings. This behaviour was observed for *soft* metals as gold and silver, in their metal complexes preferring the coordination of the nitrogen atom instead of *softer* sulphur or selenium (e.g.  $[\text{Ag}\{(n\text{-Bu})[4\text{-C}_6\text{H}_5\text{-(4H)-oxazol-5-one}\}\text{CHC}_6\text{H}_4\}\text{Se}]\text{[X]}$  ( $\text{X} = \text{OTf}, \text{PF}_6$ ,<sup>13</sup> and  $\{[\text{Ag}(\text{OTf})\}_2\{[(\text{Z})\text{-2}'\text{-}\{2\text{-C}_6\text{H}_5\text{-(4H)-oxazol-5-one}\}\text{CHC}_6\text{H}_4\}_2\text{Se}\}]\}$ ).<sup>14</sup> Due to the low solubility of the silver complexes in  $\text{CDCl}_3$ , the NMR spectra were recorded in acetone-*d*<sub>6</sub>. To have clear evidence of the coordination behaviour in the silver complexes **2** and **3**, the  $^{77}\text{Se}\{\text{^1H}\}$  NMR spectrum of **1** was measured also in acetone-*d*<sub>6</sub>. The resonance signal observed at 430 ppm for the proligand **1** suggested that the silver atoms are interacting with the selenium atoms in solution, based on the change in the chemical shift when comparing with the chemical shift for **2** and **3**.

One characteristic singlet signal for triflate ion was observed in the  $^{19}\text{F}\{\text{^1H}\}$  NMR spectrum of **2** ( $\delta = -79$  ppm), while for the  $\text{PF}_6$  anion in complex **3** a doublet resonance signal was observed at  $-72$  ppm with a  $^1J_{\text{FP}}$  coupling constant of 708 Hz.

The  $^{31}\text{P}\{\text{^1H}\}$  NMR spectrum of **3** revealed a heptet resonance signal at  $-144.28$  ppm, due to the phosphorus-fluorine coupling in the  $\text{PF}_6$  anion.

The base peaks in the ESI-HRMS were observed at  $m/z$  453.03365 for the molecular ion  $[\text{M}+\text{H}]^+$  of compound **1**, and at  $m/z$  594.95109 for the  $[\text{R}_2\text{SeAg}]^+$  cations of both compounds **2** and **3**.

Molar conductivity measurements performed in  $10^{-3}$  M acetone solution were helpful to determine the ionic nature of silver complexes (**2–3**) and the neutral nature of **4**, in solution. The  $\Lambda_{\text{M}}$  values of  $5.0 \text{ } \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$  found for the gold complex **4**, confirmed its non-electrolyte nature, while  $\Lambda_{\text{M}}$  values of  $120 \text{ } \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$  and  $150 \text{ } \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ , respectively for the silver complexes are indicating a 1 : 1 electrolyte.<sup>20</sup>

UV-Vis absorption measurements were conducted in MeOH solution ( $5\cdot 10^{-5}$  M), at room temperature, and were performed for the compound **1** and the complexes **2–4**. Table 1 displays the obtained results. For compound **1**, the absorption band appeared in the UV region at 326 nm, characterized by a large extinction coefficient. For complexes **2–4**, the absorption bands were observed in the UV region (268–274 nm). The bands observed in all compounds can be attributed to an intra-ligand charge transfer (ILCT) involving the electron-donor oxazolone ring. Notably, the absorption bands for metal complexes **2–4** were more intense than the corresponding band for compound **1** (Fig. 1).

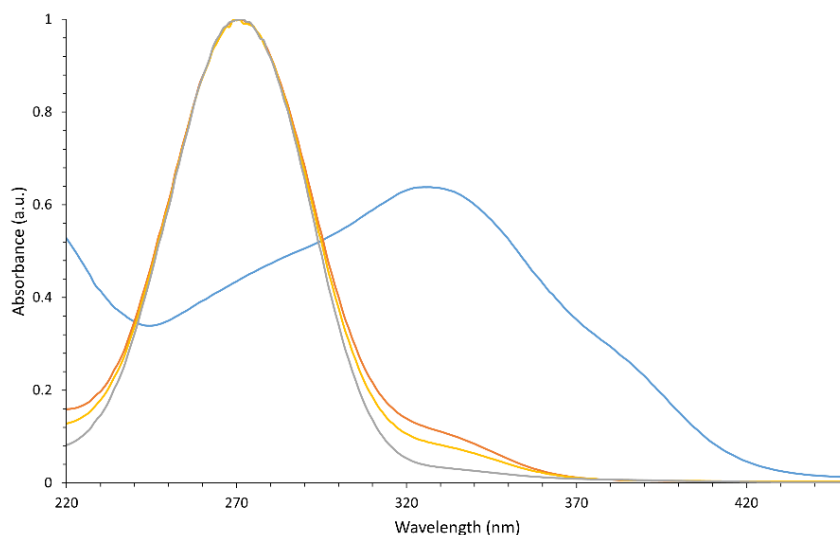


Fig. 1 – Normalized UV-vis absorption spectra of compounds **1** (blue), **2** (red), **3** (orange) and **4** (purple) (MeOH,  $5\cdot 10^{-5}$  M).

Table 1  
UV-Vis data of compounds **1–4**

Cpd.	Wavelengths (nm) [ $\epsilon$ ( $\text{M}^{-1}\cdot\text{cm}^{-1}$ )]
<b>1</b>	326 [17,858]
<b>2</b>	274 [33,480]
<b>3</b>	268 [39,456]
<b>4</b>	271 [23,126]

### Solid-state studies

The solid-state investigation of the compounds (**1–4**) was conducted by FT-IR measurements. The typical strong bands for the C=O stretching vibration in the lactone in the range of 1700–1805  $\text{cm}^{-1}$ , bands for stretching of endocyclic C=N bonds and C–O in the range of 1514–1699  $\text{cm}^{-1}$  and 1116–1373  $\text{cm}^{-1}$ , respectively were observed for all the compounds. In the IR spectrum of silver complex **2** the four characteristic bands for the triflate moiety were observed in the range 1030–

1286  $\text{cm}^{-1}$ , with a very strong band corresponding to the asymmetric  $\text{SO}_3$  stretch. The split band at 1286  $\text{cm}^{-1}$  indicates an interaction of the triflate fragment with the silver atom, in the solid state.<sup>21</sup>

The molecular structure of **1**, shown in Fig. 2, was determined by single crystal X-ray diffraction. Suitable crystals were obtained by slow evaporation of DCM solution of **1**. The geometry around the selenium atom was found to be angular with the C1–Se–C1' angle of  $96.67(2)^\circ$  and with half of the molecule being generated by symmetry.

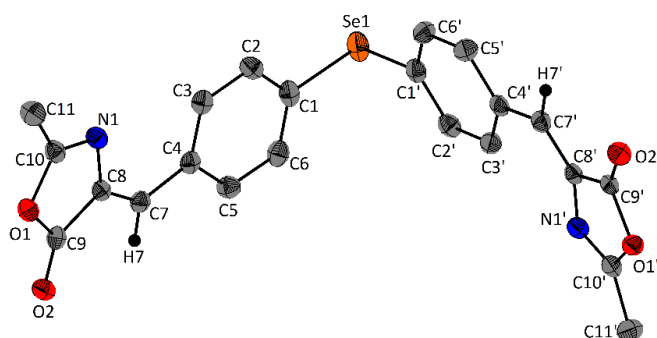


Fig. 2 – Thermal ellipsoids representation at 50% probability for **1**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): Se1–C1 1.933(3), C7–C8 1.341(4), C8–C9 1.481(4), C8–O2 1.195(4), C8–O1 1.395(4), O1–C10 1.388(4), C10–N1 1.285(4) and N1–C8 1.408(4).

In the packing of the crystal, a polymeric chain association is formed by  $\pi \cdots \pi$  interactions. The distance between the neighbouring molecules is  $\text{Cg1}(\text{O1C9C8N1C10}) \cdots \text{Cg2}'' (\text{C1-C6})$  3.75 Å, in agreement for a  $\pi \cdots \pi$  interaction,<sup>22</sup> between the

oxazolones and phenyl rings (Figure 3). The chains are further connected with other chains by  $\text{O} \cdots \pi$  interaction giving rise to a 2D network. The formation of the network being supported by  $\text{Cg1} \cdots \text{O1a}$  3.03 Å interactions (Fig. 4).

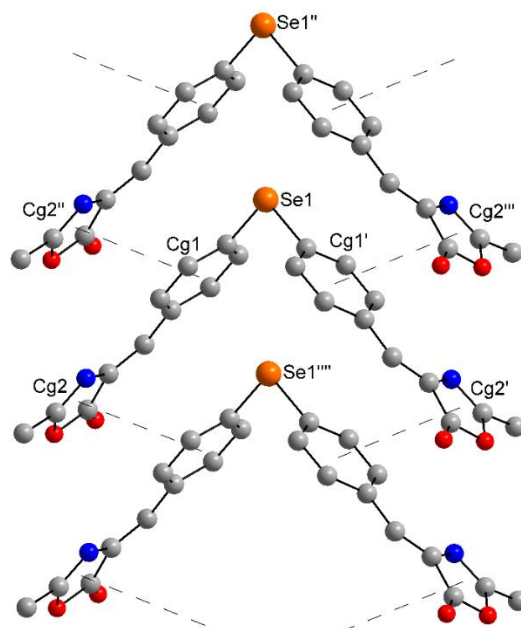


Fig. 3 – Polymeric chain association in the crystal of **1** [symmetry equivalent position  $(1-x, y, 3/2-z)$ ,  $(x, 1+y, z)$  and  $(1-x, 1+y, 3/2-z)$  are given by “prime”, “double prime” and “triple prime”]. Hydrogen atoms are omitted for clarity.

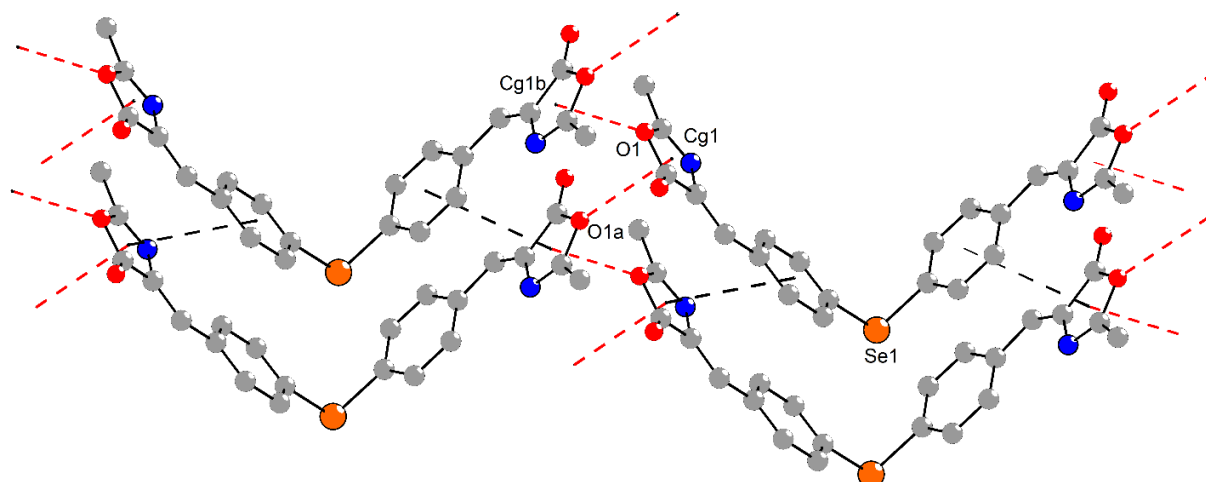


Fig. 4 – 2D network in the crystal of **1** [symmetry equivalent positions  $(1/2-x, 1/2+y, 1/2-z)$ , and  $(1/2-x, -1/2+y, 1/2-z)$  are given by “a” and “b”]. Hydrogen atoms are omitted for clarity.

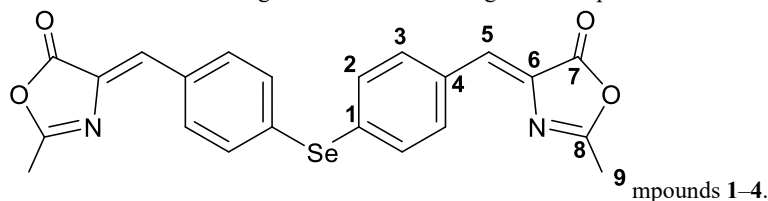
## EXPERIMENTAL

### General experimental information

The commercially available *N*-acetyl glycine, sodium acetate, AgOTf and AgPF<sub>6</sub> were used with no additional purification, while [4-(O=CH)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>Se,<sup>14</sup> and AuCl(tht)<sup>23</sup> were prepared following literature methods. The solvents used for the preparation of the ligand and complexes were distilled and dried following standard procedures. Multinuclear NMR spectra (<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>77</sup>Se{<sup>1</sup>H}, <sup>19</sup>F{<sup>1</sup>H}, <sup>31</sup>P{<sup>1</sup>H}) and 2D NMR spectra were recorded at room temperature, in CDCl<sub>3</sub> and acetone-*d*<sub>6</sub> on Bruker Avance 400 and 600, respectively operating at 400.13 MHz (<sup>1</sup>H), 100.62 MHz (<sup>13</sup>C{<sup>1</sup>H}), 76.31 MHz (<sup>77</sup>Se{<sup>1</sup>H}) and 600 MHz (<sup>1</sup>H), 151 MHz (<sup>13</sup>C{<sup>1</sup>H}), 376 MHz (<sup>19</sup>F{<sup>1</sup>H}) and 162 MHz (<sup>31</sup>P{<sup>1</sup>H}). The chemical shifts are reported in δ units (ppm) relative to TMS (<sup>1</sup>H,

<sup>13</sup>C{<sup>1</sup>H}),<sup>21</sup> Me<sub>2</sub>Se (<sup>77</sup>Se{<sup>1</sup>H}), trifluoroacetic acid (<sup>19</sup>F{<sup>1</sup>H}) and H<sub>3</sub>PO<sub>4</sub> 85% (<sup>31</sup>P{<sup>1</sup>H}).<sup>24</sup> The NMR data were handled with the Mestre Nova software.<sup>25</sup> The assignments of the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} chemical shifts are based on 2D NMR correlation experiments (*e.g.* COSY, HSQC and HMBC) and are given according to the numbering scheme depicted in Scheme 2. ESI mass spectra were recorded with a Thermo Scientific LTQ-OrbitrapXL instrument equipped with a standard ESI/APCI source. Molar conductivities measurements of 10<sup>-3</sup> M solutions in acetone were performed with a TDS Meter CON 510 conductometer. The UV-vis experiments were conducted on a Cary 60 UV-Vis spectrophotometer (Agilent) in the range of 200–900 nm for MeOH HPLC grade 10<sup>-5</sup> M solutions. Infrared spectra were performed on a Bruker Vector 2 instrument. Melting points were determined with an Electrothermal 9200 apparatus.

Scheme 2 – The numbering scheme for NMR assignments in precursors and co



*Synthesis of [(Z)-4'-{2-CH<sub>3</sub>-(4H)-oxazol-5-one}CHC<sub>6</sub>H<sub>4</sub>]<sub>2</sub>Se (**1**).* A mixture containing [4-(O=CH)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>Se (0.470 g, 1.63 mmol), *N*-acetyl glycine (0.381 g, 3.25 mmol), anhydrous sodium acetate (0.533 g, 6.5 mmol) and 2 mL of acetic anhydride was refluxed for 4 hours at 100°C. The

mixture was allowed to cool down to room temperature and the compound was precipitated using cold EtOH. After filtering the suspension, an intense yellow solid was isolated and was washed several times with cold EtOH. Yield = 0.262 g (36%). M.p. 185°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ

7.98 (d,  $^3J_{HH} = 8.3$  Hz, 4H, H-3), 7.51 (d,  $^3J_{HH} = 8.4$  Hz, 4H, H-2), 7.09 (s, 2H, H-5), 2.40 (s, 6H, H-9) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.64 (C-7), 166.36 (C-8), 135.10 (C-6), 133.00 (C-2), 132.92 (C-4), 132.83 (C-3), 132.43 (C-1), 130.32 (C-5), 15.76 (C-9) ppm.  $^{77}\text{Se}\{^1\text{H}\}$  NMR (114 MHz,  $\text{CDCl}_3$ ):  $\delta$  436 ppm.  $^{77}\text{Se}\{^1\text{H}\}$  NMR (114 MHz, acetone- $d_6$ ):  $\delta$  430 ppm. HRMS (APCI+, MeCN),  $m/z$  (%): 453.03365 (100),  $[\text{M}+\text{H}]^+$ , calcd. for  $\text{C}_{22}\text{H}_{17}\text{N}_2\text{O}_4\text{Se}$ :  $m/z = 453.03481$ . IR (KBr pellet,  $\nu$ ,  $\text{cm}^{-1}$ ): 1805 (s)/1777 (s)  $[\nu(\text{C}=\text{O})]$ , 1683 (s)  $[\nu(\text{C}=\text{N})]$ , 1606 (m), 1421 (m), 1229 (s), 1161 (s)  $[\nu(\text{C}-\text{O})]$ , 903 (m), 819 (w), 762 (w), 628 (w), 562 (w).  $A_m = 0.61 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ .

*Synthesis of  $[\text{Ag}\{(\text{Z})-4'-\{2-\text{CH}_3-(4\text{H})\text{-oxazol-5-one}\}\text{CHC}_6\text{H}_4\}_2\text{Se}][\text{OTf}]$  (2).* Silver triflate (0.057 g, 0.22 mmol) was added to a solution of compound **1** (0.1 g, 0.22 mmol) in 30 mL of acetone. After stirring for an hour at room temperature, in the absence of light, the solvent was removed in vacuum. After washing the compound with  $\text{Et}_2\text{O}$  ( $3 \times 15$  mL) a deep red solid was isolated. Yield = 0.149 g (95%). M. p.  $152^\circ\text{C}$  (dec.).  $^1\text{H}$  NMR (400 MHz, acetone- $d_6$ ):  $\delta$  7.63 (d,  $^3J_{HH} = 8.4$  Hz, 4H, H-3), 7.57 (d,  $^3J_{HH} = 8.4$  Hz, 4H, H-2), 7.32 (s, 2H, H-5), 2.07 (s, 6H, H-9) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, acetone- $d_6$ ):  $\delta = 169.58$  (C-8), 166.44 (C-7), 135.25 (C-6), 133.80 (C-3), 131.83 (C-3), 131.23 (C-5), 127.94 (C-4), 127.79 (C-1), 23.00 (C-9) ppm.  $^{19}\text{F}\{^1\text{H}\}$  NMR (376 MHz, acetone- $d_6$ ):  $\delta = -79$  ppm.  $^{77}\text{Se}\{^1\text{H}\}$  NMR (76 MHz, Acetone- $d_6$ ):  $\delta = 409$  ppm. HRMS (ESI+, MeOH),  $m/z$  (%): 594.95109 (100),  $[\text{C}_{23}\text{H}_{23}\text{O}_5\text{N}_2\text{AgSe}]^+$ , calcd. for  $\text{C}_{23}\text{H}_{23}\text{O}_5\text{N}_2\text{AgSe}$ :  $m/z = 594.95320$ . IR (KBr pellet,  $\nu$ ,  $\text{cm}^{-1}$ ): 1715 (s)/1633 (s)  $[\nu(\text{C}=\text{O})]$ , 1583 (m)  $[\nu(\text{C}=\text{N})]$ , 1606 (m), 1421 (m), 1229 (s), 1375 (s)  $[\nu(\text{C}-\text{O})]$ , 1252 (s) / 1166 (m)  $[\nu(\text{C}-\text{O})]$ , 1030 (m), 817 (w), 638 (w), 520 (w).  $A_m = 120 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ .

*Synthesis of  $[\text{Ag}\{(\text{Z})-4'-\{2-\text{CH}_3-(4\text{H})\text{-oxazol-5-one}\}\text{CHC}_6\text{H}_4\}_2\text{Se}][\text{PF}_6]$  (3).* Silver hexafluorophosphate (0.056 g, 0.22 mmol) was added to a solution of compound **1** (0.1 g, 0.22 mmol) in 40 mL of acetone. After stirring for an hour at room temperature, in the absence of light, the solvent was removed, and the red solid was isolated after washing with  $\text{Et}_2\text{O}$  ( $3 \times 15$  mL). Yield = 0.147 g (94%). M. p.  $145^\circ\text{C}$  (dec.).  $^1\text{H}$  NMR (600 MHz, acetone- $d_6$ ):  $\delta$  7.63 (d,  $^3J_{HH} = 8.0$  Hz, 4H, H-3), 7.56 (d,  $^3J_{HH} = 8.0$  Hz, 4H, H-2), 7.32 (s, 2H, H-5), 2.07 (s, 6H, H-9) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, acetone- $d_6$ ):  $\delta$  169.55 (C-7), 166.47 (C-8),

135.30 (C-6), 133.77 (C-3), 131.85 (C-2), 131.25 (C-5), 127.89 (C-4), 127.74 (C-1), 23.04 (C-9).  $^{19}\text{F}\{^1\text{H}\}$  NMR (376 MHz, acetone- $d_6$ ):  $\delta = -71.63$  (d,  $^1J_{FP} = 708$  Hz) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz, acetone- $d_6$ ):  $\delta -144.28$  (hept,  $^1J_{FP} = 708$  Hz) ppm.  $^{77}\text{Se}\{^1\text{H}\}$  NMR (76 MHz, acetone- $d_6$ ):  $\delta$  393 ppm. HRMS (ESI+, MeOH),  $m/z$  (%): 594.95109 (98),  $[\text{C}_{23}\text{H}_{23}\text{O}_5\text{N}_2\text{AgSe}]^+$ , calcd. for  $\text{C}_{23}\text{H}_{23}\text{O}_5\text{N}_2\text{AgSe}$ :  $m/z = 594.95320$ . IR (KBr pellet,  $\nu$ ,  $\text{cm}^{-1}$ ): 1805 (s)/1775 (s)  $[\nu(\text{C}=\text{O})]$ , 1699 (m)  $[\nu(\text{C}=\text{N})]$ , 1580 (m), 1420 (m), 1312 (s)  $[\nu(\text{C}-\text{O})]$ , 1160 (m), 1010 (m), 903 (m), 817 (w), 762 (w), 702 (w), 628 (w).  $A_m = 150 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ .

*Synthesis of  $[\text{AuCl}\{(\text{Z})-4'-\{2-\text{CH}_3-(4\text{H})\text{-oxazol-5-one}\}\text{CHC}_6\text{H}_4\}_2\text{Se}]$  (4).* AuCl(tht) (0.071 g, 0.22 mmol) was added to a solution of compound **1** (0.1 g, 0.22 mmol) in 30 mL of chloroform. After stirring for an hour at room temperature, the solvent was removed under vacuum. After washing the compound with hexanes ( $3 \times 25$  mL) an orange solid was isolated. Yield = 0.145 mg (96%). M.p.  $139^\circ\text{C}$  (dec.).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.99 (d,  $^3J_{HH} = 8.4$  Hz, 4H, H-3), 7.52 (d,  $^3J_{HH} = 8.5$  Hz, 4H, H-2), 7.09 (s, 2H, H-5), 2.40 (s, 6H, H-9) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.75 (C-7), 166.51 (C-8), 135.09 (C-6), 133.14 (C-3), 133.09 (C-4), 132.96 (C-2), 132.63 (C-1), 130.39 (C-5), 15.88 (C-9) ppm.  $^{77}\text{Se}\{^1\text{H}\}$  NMR (76 MHz,  $\text{CDCl}_3$ ):  $\delta = 436$  ppm. HRMS (ESI+, DCM, MeOH),  $m/z$  (%): 648.99353 (40),  $[\text{M}-\text{Cl}]^+$ , calcd. for  $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_4\text{SeAu}$ :  $m/z = 649.11206$ . IR (KBr pellet,  $\nu$ ,  $\text{cm}^{-1}$ ): 1700 (s)/1650 (s)  $[\nu(\text{C}=\text{O})]$ , 1539 (m)  $[\nu(\text{C}=\text{N})]$ , 1420 (m), 1315 (m)  $[\nu(\text{C}-\text{O})]$ , 1008 (s), 849 (s), 704 (w), 635 (w).  $A_m = 5.0 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ .

### Crystal structure determination

The crystal of **1** was mounted on MiTeGen microMounts cryoloops and data were collected on a Bruker D8 VENTURE diffractometer using Mo- $K\alpha$  radiation ( $\lambda = 0.71073$  Å) from an I $\mu$ S 3.0 microfocus source with multilayer optics, at 100 K. For structure solving and refinement, the Bruker APEX5 Software Package was used.<sup>26</sup> Hydrogen atoms were placed in fixed, idealized positions and refined with a riding model and a mutual isotropic thermal parameter. The structure was refined with anisotropic thermal parameters for non-H atoms. The drawings were created using the Diamond program<sup>27</sup> and the intermolecular contacts were found in Platon.<sup>22</sup> Table 2 contain the details of the crystal structure determination and refinement.

Table 2

Crystal data and structure refinement for compound <b>1</b>	
Empirical formula	C <sub>22</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub> Se
Formula weight	451.33
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	C2/c
Unit cell dimensions	a = 27.0002(17) Å    α = 90° b = 4.8771(2) Å    β = 125.070(2)° c = 17.5677(11) Å    γ = 90°
Volume	1893.37(19) Å <sup>3</sup>
Z	4
Density (calculated)	1.583 Mg/m <sup>3</sup>
Absorption coefficient	2.016 mm <sup>-1</sup>
F(000)	912
Crystal size	0.218 × 0.231 × 0.327 mm <sup>3</sup>
Theta range for data collection	2.33 to 28.32°
Reflections collected	24361
Independent reflections	2365 [R(int) = 0.0989]
Completeness to theta = 28.31°	100%
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	2365 / 0 / 133
Goodness-of-fit on F <sup>2</sup>	1.062
Final R indices [I > 2σ(I)]	R1 = 0.0512, wR2 = 0.0926
R indices (all data)	R1 = 0.0797, wR2 = 0.1027
Largest diff. peak and hole	1.450 and -0.442 e.Å <sup>-3</sup>
CCDC No.	<b>2456225</b>

## CONCLUSIONS

Key insights into the coordination behavior of the diorganoselenide ligand in the metal complexes were provided by <sup>77</sup>Se{<sup>1</sup>H} NMR spectra. The identical chemical shift for proligand **1** and complex **4** suggests that the gold atom in complex **4** is coordinated by the nitrogen atoms of the oxazolone rings, while the notable chemical shift change for proligand **1** when compared to complexes **2** and **3** indicates that the silver atoms are coordinated by the selenium atoms.

As suggested from the characterization data, the silver complexes **2** and **3** are ionic species in solution, while in solid state the triflate fragment is bonded to the silver atom in complex **2**.

The packing of the crystal in **1** revealed the formation of a supramolecular 2D architecture, sustained by π···π and O···π interactions.

Both proligand **1** and the metal complexes display strong absorption bands with high molar extinction coefficients in the UV-Vis absorption spectra. These bands are due to the intraligand charge transfer (ILCT) effect originating from the oxazolone rings. Complexes **2–4** exhibit a hypsochromic shift relative to compound **1**, with modification in the intensity of the bands.

*Supplementary material.* CCDC 2456225 contain the supplementary crystallographic data for compound **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

*Acknowledgments.* This work was supported by a grant of the Roumanian Ministry of Education and Research, CNCS – UEFISCDI, project number PN-IV-PCE-0966 / 2025.

## REFERENCES

- V. Lippolis, C. Santi, E. J. Lenardão and A. L. Braga (Eds.), "Chalcogen Chemistry: fundamentals, advances and application", RSC, Cambridge, UK, 2023.
- R. Laitinen and R. Oilunkaniemi (Eds.), "Selenium and Tellurium Reagents in Chemistry and Materials Science", Walter de Gruyter GmbH: Berlin, Germany; Boston, MA, USA, 2019.
- A. Arora, S. Singh, P. Oswal, D. Nautiyal, G. K. Rao, S. Kumar, A. Kumar, *Coord. Chem. Rev.* **2021**, 438, 213885.
- A. Singh, A. Kaushik, J. S. Dhau, R. Kumar, *Coord. Chem. Rev.* **2022**, 450, 214254.
- L. Zhang, F. A. Christie, A. E. Tarcza, H. G. Lancaster, L. J. Taylor, M. Bühl, O. L. Malkina, J. D. Woollins, C. L. Carpenter-Warren, D. B. Cordes, A. M. Z. Slawin, B. A. Chalmers, P. Kilian, *Inorg. Chem.* **2023**, 62, 16084–16100.

6. B. G. Singh, Amit Kunwar, *Free Radical Res.* **2021**, *55*, 873–886.
7. M. A. Abbady, M. M. Aly, M. T. Ismail, Sh. H. Abdel-Hafez, *Phosphorus, Sulfur, and Silicon* **2015**, *190*, 1828–1844.
8. A. A. Lysova, R. D. Marchenko, D. G. Samsonenko, A. S. Potapov, V. P. Fedina, *Russ. Chem. Bull.* **2020**, *69*, 1122–1129.
9. E. Laga, D. Dalmau, S. Arregui, O. Crespo, A. I. Jimenez, A. Pop, C. Silvestru, E. P. Urriolabeitia, *Molecules* **2021**, *26*(5), 1238.
10. C. Garcia-Sanz, A. Andreu, B. de las Rivas, A. I. Jimenez, A. Pop, C. Silvestru, E. P. Urriolabeitia, J. M. Palomo, *Org. Biomol. Chem.* **2021**, *19*, 2773–2783.
11. S. Collado, A. Pueyo, C. Baudequin, L. Bischoff, A. I. Jiménez, C. Cativiela, C. Hoarau, E. P. Urriolabeitia, *Eur. J. Org. Chem.* **2018**, 6158–6166.
12. D. Dumitraș, D. Dalmau, P. García-Orduña, A. Pop, A. Silvestru, E. P. Urriolabeitia, *Dalton Trans.* **2024**, *53*, 8948–8957.
13. R. A. Butuza, D. Dumitras, C. Bohan, A. Pop, *New J. Chem.* **2023**, *47*, 2202–2210.
14. D. Dumitras, E. Gal, C. Silvestru, A. Pop, *Molecules* **2024**, *29*(4), 792.
15. A. Pop, D. Rosca, R. Mitea, A. Silvestru, *Inorg. Chim. Acta* **2013**, *405*, 235–242.
16. R. A. Popa, A. Silvestru, A. Pop, *Polyhedron* **2016**, *110*, 197–202.
17. A. Pop, A. Silvestru, E. J. Juárez-Pérez, M. Arca, V. Lippolis, C. Silvestru, *Dalton Trans.* **2014**, *43*, 2221.
18. J. S. Buck, W. S. Ide, *Org. Synth.* **1933**, *13*, 8–9.
19. M. Blanco-Lomas, P.J. Campos, D. Sampedro, *Org. Lett.* **2012**, *14*, 4334–4337.
20. W. J. Geary, *Coord. Chem. Rev.* **1971**, *7*, 81–122.
21. S. J. Angus-Dunne, L. E. P. Lee Chin, R. C. Burns, G. A. Lawrance, *Transition Met. Chem.* **2006**, *31*, 268–275.
22. A. L. Spek, *J. Appl. Cryst.* **2003**, *36*, 7–13.
23. R. Uson, A. Laguna and M. Laguna, *Inorg. Synth.* **1989**, *26*, 85.
24. G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176–2179.
25. MestReC; MestReNova; Mestrelab Research S.L. A Coruna 15706, version 14; Mestrelab Research: Santiago de Compostela, Spain, **2020**.
26. G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.* **2015**, *C71*, 3–8.
27. DIAMOND – Visual Crystal Structure Information System, CRYSTAL IMPACT, Postfach 1251, 53002 Bonn, Germany, **2001**.