

*Dedicated to Prof. Ion Grosu
on the occasion of his 70th anniversary*

SYNTHESIS, CHARACTERIZATION AND REACTIVITY OF [(Z)-2'-{2-C₆H₅-(4H)-OXAZOL-5-ONE}CHC₆H₄]₂Se₂

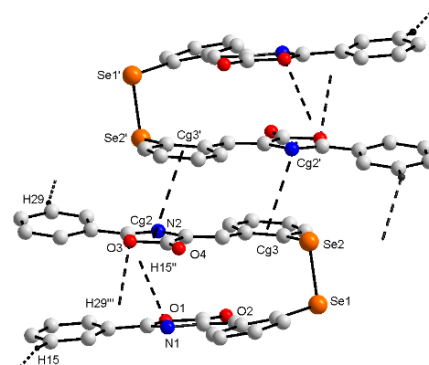
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Novel [(Z)-2'-{2-C₆H₅-(4H)-oxazol-5-one}CHC₆H₄]₂Se₂ (**1**) was obtained, structurally characterized, both in solution and in solid state, and the reactivity was investigated in reactions with MCl₂ (M = Zn, Cd and Hg). Compound **1** and the metal complexes [ZnCl₂{[(Z)-2'-{2-C₆H₅-(4H)-oxazol-5-one}CHC₆H₄]₂Se₂}] (**2**), [CdCl₂{[(Z)-2'-{2-C₆H₅-(4H)-oxazol-5-one}CHC₆H₄]₂Se₂}] (**3**) and [HgCl₂{[(Z)-2'-{2-C₆H₅-(4H)-oxazol-5-one}CHC₆H₄]₂Se₂}] (**4**) displays similar photophysical properties, the presence of oxazolone rings on the phenyl substituents, covalently bonded to the selenium atoms, induced a bathochromic shift in the UV-Vis spectra of the investigated compounds. The supramolecular architecture supported by intermolecular C–H⋯O and π⋯π interactions was observed in solid state by single crystal X-ray diffraction studies.



INTRODUCTION

Organoselenium compounds are a class of important selenium derivatives, intensively studied by researchers, due to their well-established use in many applicative research fields.¹ One of the interests in such compounds being the development of metal selenides with optical properties for material science,² and/or organoselenium sensors for detecting biologically

important analytes.^{3–6} The design of fluorescent sensors for heavy metal ion detection, which involves adding a fluorophore fragment to a selenide scaffold, has led to their increased popularity due to their high selectivity and sensitivity. For example diselenide containing coumarin-based probe was found to selectively detect Hg(II),⁷ or selenium containing anthracene derivatives displayed selective chelation enhanced fluorescence with Hg(II).⁸

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Appreciating that oxazolones are a class of compounds with good optical properties,^{9,10} we have obtained a new diorganodiselenide containing 5-(4*H*)-oxazolones fragments, using [2-(O=CH)C₆H₄]₂Se₂,¹¹ as a precursor, thus extending our recent studies regarding homoleptic and heteroleptic diorganoselenides [e.g. [(*Z*)-2'-{2-C₆H₅-(4*H*)-oxazol-5-one}CHC₆H₄]₂Se,¹² and (*n*-Bu)[(*Z*)-4'-{2-C₆H₅-(4*H*)-oxazol-5-one}CHC₆H₄]₂Se.¹³ Our primary focus being the fundamental aspects of coordination chemistry, we have synthesized and thoroughly characterized the target molecule [(*Z*)-2'-{2-C₆H₅-(4*H*)-oxazol-5-one}CHC₆H₄]₂Se₂. We then employed this molecule as a ligand with group 11 metals salts and investigated the optical properties of the resulting metal complexes.

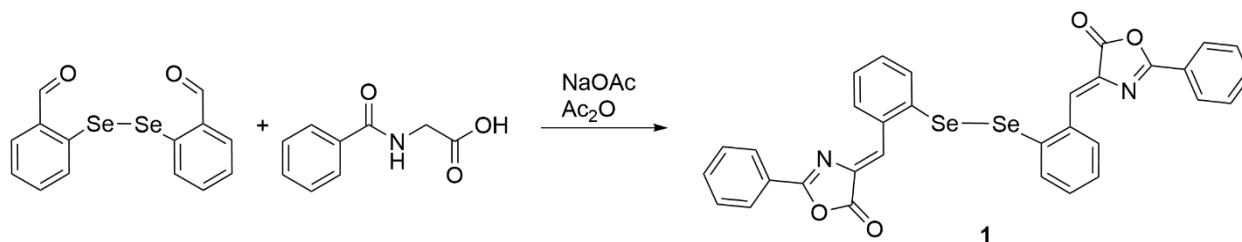
RESULTS

Using the Erlenmeyer-Plöchl method,¹⁴ [(*Z*)-2'-{2-C₆H₅-(4*H*)-oxazol-5-one}CHC₆H₄]₂Se₂ (**1**) was prepared by reacting at 100 °C for 2 h, [2-(O=CH)C₆H₄]₂Se₂,¹¹ with *N*-benzoylglycine, in the presence of sodium acetate (1:2:4 molar ratio) in acetic anhydride. After working up the reaction mixture in open atmosphere, the target compound

was isolated as orange solid in very good yields (80%). Using this method, as previously observed in the literature, only the *Z* isomer was isolated.¹⁵ The [2-(O=CH)C₆H₄]₂Se₂ precursor, reported in the literature¹¹ was obtained by the lithiation of the freshly prepared 2-[(CH₂O)₂CH]C₆H₄Br, following the method described in our group.¹⁶

The reactivity compound **1** was investigated by complexation reactions with MCl₂ (M = Zn, Cd, Hg) in 1 : 1 molar ratio, at room temperature, in THF. [ZnCl₂{[(*Z*)-2'-{2-C₆H₅-(4*H*)-oxazol-5-one}CHC₆H₄]₂Se₂}] (**2**), [CdCl₂{[(*Z*)-2'-{2-C₆H₅-(4*H*)-oxazol-5-one}CHC₆H₄]₂Se₂}] (**3**) and [HgCl₂{[(*Z*)-2'-{2-C₆H₅-(4*H*)-oxazol-5-one}CHC₆H₄]₂Se₂}] (**4**), were isolated as intense yellow solids, in very good yields.

Diorganodiselenide **1** and the new metal complexes **2–4** were characterized in solution by multinuclear NMR spectroscopy, mass spectrometry and molar conductivities, and in the solid state by IR spectroscopy and the molecular structure of **1** was determined by single crystal X-Ray diffraction. The optical properties of the compounds were investigated in solution by UV-Vis measurements.



Scheme 1 – Synthesis of compound **1**.

DISCUSSION

The ¹H NMR and ¹³C{¹H} NMR spectra of compound **1** and complexes **2–4**, respectively showed only one set of resonances for the organic groups, slightly shifted in the metal complexes when compared with the free proligand **1**, suggesting that the two organic groups are equivalent.

The aromatic regions in the ¹H NMR spectra of the compounds **1–4** displayed the resonance signals with the expected multiplicity for the aromatic protons. The formation of the 5-membered heterocycle in compounds **1** was also confirmed by the chemical shift of the singlet resonances for protons H-7, changing from 10.19 ppm in [2-(O=CH)C₆H₄]₂Se₂ to around 7.6 ppm in compounds **1–4**. The presence of only one set of signals for the

protons in the ¹H NMR spectra of metal complexes **2–4** suggest a fast change in coordination of the metal from one organic group to the other.

The ⁷⁷Se{¹H} NMR spectra showed one singlet signal at 475 ppm for **1**, shifted when comparing to the [2-(O=CH)C₆H₄]₂Se₂ precursor (δ 456 ppm). The same chemical shift for **2–4** in the ⁷⁷Se{¹H} NMR spectra (δ = 476 ppm) suggested that the metals in complexes **2–4** are bounded by the nitrogen atoms in the oxazolone rings. The observed preference of some *soft* metals for nitrogen coordination over selenium coordination is consistent with previous findings for several silver, gold, and zinc complexes (e.g. [Ag{(n-Bu)[4-C₆H₅-(4*H*)-oxazol-5-one}CHC₆H₄]₂Se][X] (X = OTf, PF₆,¹³ and [ZnCl₂(*Z*)-2'-{2-C₆H₅-(4*H*)-oxazol-5-one}CHC₆H₄]₂Se]¹²). Moreover, in solid state, it was observed for [{Ag(OTf)}₂{[(*Z*)-2'-{2-C₆H₅-

(4*H*)-oxazol-5-one}CHC₆H₄]₂Se}] that the diorganoselenium ligand coordinates to the silver atom only through the nitrogen atom from one oxazolone ring.¹²

The APCI+ HRMS spectra shows the base peak at *m/z* 327.98713 [RSe⁺] (R = (*Z*)-2'-{2-C₆H₅-(4*H*)-oxazol-5-one}CHC₆H₄) for compound **1**, while in ESI+ HRMS for complex **2** a peak corresponding to [M-Cl₂]⁺ at *m/z* 719.06111 was observed.

Molar conductivity measurements were performed in 10⁻³ M DMSO solution to confirm the neutral nature of the complexes. The Λ_M values in the range 0.45–2.65 Ω⁻¹·cm²·mol⁻¹ found for the complexes **2–4**, indicate their non-electrolyte nature.¹⁷

UV-Vis absorption measurements for [2-(O=CH)C₆H₄]₂Se₂ precursor, compound **1** and the

metal complexes **2–4** were performed in CH₂Cl₂ solution (5·10⁻⁵ M), at room temperature. The obtained results are listed in Table 1.

The UV-Vis spectra of the compounds revealed the absorption bands from UV regions (240–345 nm) assigned to the π–π* electronic transition. A higher energy band characterized by large extension coefficient in the visible region of the spectra was attributed to the electron donor oxazolone ring by intra-ligand charge transfer (ILCT) (Fig.1a) for **1** and the metal complexes. The pattern of the bands for the metal complexes are similar to those of the free proligand **1**, showing no change in intensity (Figure 1b), thus suggesting that M···M interactions are not present in solution.

Table 1

UV-Vis data of compounds 1–4

| Cpd. | Wavelengths (nm) [ε (M ⁻¹ ·cm ⁻¹)] |
|---|--|
| [2-(O=CH)C ₆ H ₄] ₂ Se ₂ | 241 (sh); 271 (sh); 345 [7655] |
| 1 | 246 (sh); 367 [38,324]; 400 (sh) |
| 2 | 254 [198,473]; 260 (sh); 359 [249,136]; 360 (sh); 400 (sh) |
| 3 | 249 [5381]; 260(sh); 360 (sh); 372 [107,729]; 400 (sh) |
| 4 | 253 [91,811]; 260 (sh); 360 (sh); 372 [85,781]; 400 (sh) |

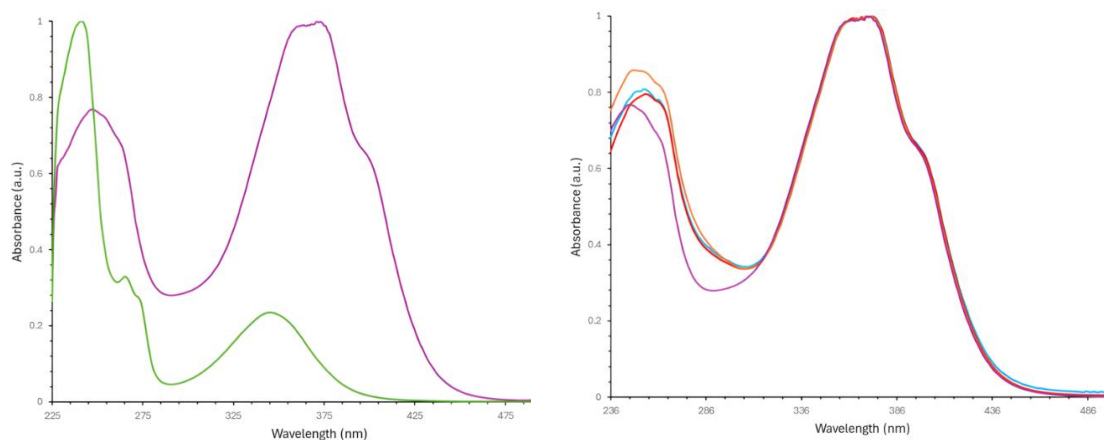


Fig. 1 – a) Normalized UV-Vis absorption spectra of compounds [2-(O=CH)C₆H₄]₂Se₂ ((green) and compound **1** (purple) (CH₂Cl₂, 5·10⁻⁵ M); b) UV-Vis spectra of compounds **1** (purple), **2** (red), **3** (orange) and **4** (blue) (CH₂Cl₂, 5·10⁻⁵ M).

Suitable crystals for X-ray diffraction investigation were obtained by slow diffusion of *n*-hexane into concentrated dichloromethane solution of **1**, relevant bond distances and angles are given in Table 2. The molecular structure (Fig. 2), shows a bent geometry around the selenium atoms with C1-Se1-Se2 angle of 101.63(5)° and C17-Se2-Se1 angle of 104.78(5)°, respectively with a skewed structure, as observed for bis(2-amino-5-benzoylphenyl)diselenide [C1-Se1-Se2 angle of 97.2° and C14-Se2-Se1 angle of 99.2°,¹⁸ respectively]. The organic substituents attached to the

selenium atoms are not planar (deviations of atoms from the best plane of a [2'-{2-C₆H₅-(4*H*)-oxazol-5-one}CHC₆H₄]Se fragment range between 0.20(1) Å for C9 and 1.71(1) Å for C10 and 0.35(1) Å for N2 and 1.51(1) Å for O3, respectively). The distance between the two oxazolone rings Cg1(O1C9C8N1C10)···Cg2(O3C24C23N2C25) is 3.7296(1) Å in the range of a π···π interaction, *cf.* Cg···Cg < 6.0 Å.¹⁹ Further intermolecular interactions linking Cg3(C17-C22) and Cg2' [Cg3···Cg2' 3.7094(1) Å *cf.* Cg···Cg < 6.0 Å]¹⁹ between two

neighbouring molecules, give rise to a dimeric association (Fig. 3). With the support of hydrogen contacts [O1...H15'' 2.69 Å and O3...H29''' 2.69 Å, *cf.*

$\Sigma r_{vdw}(O,H) 2.85 \text{ \AA}]^{20}$ the supramolecular 3D architecture is sustained in the packing of the crystal (Fig. 4).

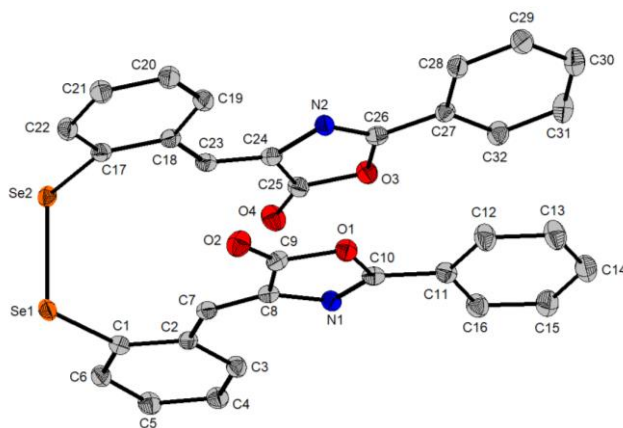


Fig. 2 – Thermal ellipsoids representation at 50% probability for **1**. Hydrogen atoms are omitted for clarity.

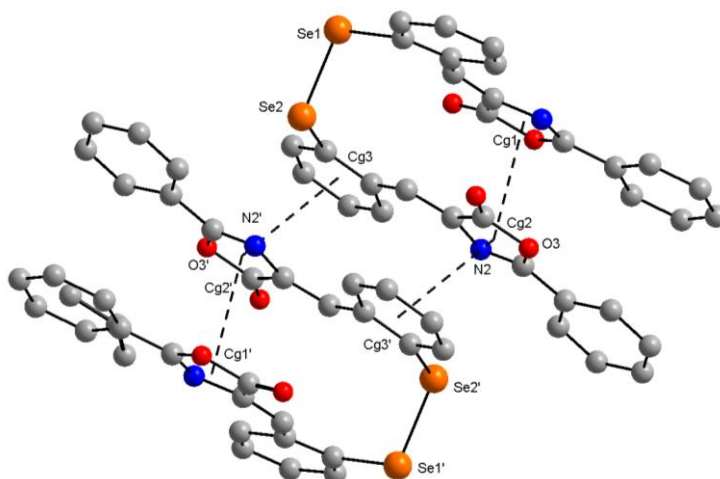


Fig. 3 – Dimeric association in the crystal of **1** [symmetry equivalent position $(-x, 1-y, 1-z)$ is given by “prime”]. Hydrogen atoms are omitted for clarity.

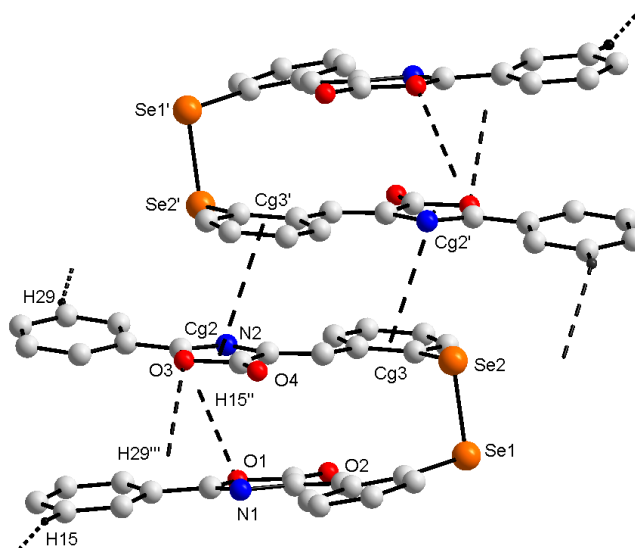


Fig. 3 – O...H interactions in the crystal of **1** [symmetry equivalent positions $(-x, 1-y, 1-z)$, $(x, 1/2-y, -1/2+z)$ and $(x, 1/2-y, 1/2+z)$ are given by “prime”, “double prime” and “triple prime”]. Only hydrogen atoms involved in interactions are shown.

Table 2

Selected bond distances Å and angles ° in compound **1**

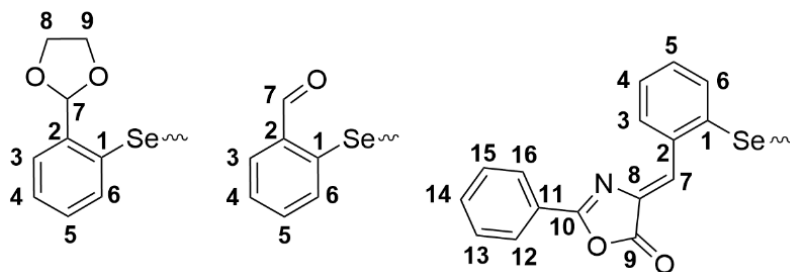
| | | | |
|------------|------------|-------------|------------|
| Se1-Se2 | 2.3435(2) | Se2-C17 | 1.9348(16) |
| Se1-C1 | 1.9323(16) | C24-C25 | 1.482(2) |
| C8-C9 | 1.481(2) | C25-O4 | 1.188(2) |
| C9-O2 | 1.193(2) | C25-O3 | 1.408(2) |
| C9-O1 | 1.403(2) | O3-C26 | 1.3772(98) |
| O1-C10 | 1.3813(19) | C26-N2 | 1.293(2) |
| C8-N1 | 1.401(2) | C24-N2 | 1.400(2) |
| C10-N1 | 1.290(2) | | |
| C1-Se1-Se2 | 101.63(5) | C17-Se2-Se1 | 104.78(5) |
| O2-C9-O1 | 122.07(15) | C24-C25-O4 | 133.79(16) |
| C9-O1-C10 | 105.42(12) | C24-C25-O3 | 104.17(13) |
| O1-C10-N1 | 116.48(15) | C25-O3-C26 | 105.60(12) |
| C10-N1-C8 | 105.30(13) | O3-C26-N2 | 116.36(14) |
| N1-C8-C9 | 108.42(1) | C26-N2-C24 | 105.45(13) |
| C8-C9-O2 | 133.46(14) | N2-C24-C25 | 108.42(14) |
| C8-C9-O1 | 104.36(13) | O4-C25-O3 | 122.03(15) |

EXPERIMENTAL

General experimental information

The starting materials, 2-(CHO)C₆H₄Br, ⁿBuLi, *N*-benzoylglycine, sodium acetate, Se, ZnCl₂, CdCl₂, HgCl₂ were commercially available and were used with no additional purification. 2-[(CH₂O)₂CH]C₆H₄Br and [2-(O=CH)C₆H₄]₂Se₂,¹⁶ were prepared following literature methods. The solvents used for the preparation of the ligand were dried and distilled under argon atmosphere by following standard procedures. All the compounds were structurally characterized both in solution and in solid state. Multinuclear NMR spectra (¹H, ¹³C{¹H}, ⁷⁷Se{¹H}) and 2D NMR spectra were recorded at room temperature, in CDCl₃ on Bruker Avance 400 operating at 400.13 MHz (¹H), 100.62 MHz (¹³C{¹H}), 76.31 MHz (⁷⁷Se{¹H}). The chemical shifts are reported in δ units (ppm) relative

to TMS (¹H, ¹³C{¹H}),²¹ Me₂Se (⁷⁷Se{¹H}).²¹ The NMR data were processed using the Mestre Nova software.²² The assignments of the ¹H and ¹³C{¹H} chemical shifts are based on 2D NMR correlation experiments (i.e. COSY, HSQC and HMBC) and are given according to the numbering depicted in Scheme 2. ESI and APCI mass spectra were performed with a Thermo Scientific LTQ-OrbitrapXL instrument equipped with a standard ESI/APCI source. Molar conductivities of 10⁻³ M solutions in DMSO were conducted with a TDS Meter CON 510 conductometer. The UV-vis measurements were carried out on a Cary 60 UV-Vis spectrophotometer (Agilent) in the range of 200–900 nm for CH₂Cl₂ HPLC grade 10⁻⁵ M solutions. Infrared spectra were recorded on a JASCO FT/IR-615 instrument. Melting points were measured on an Electrothermal 9200 apparatus. Elemental analyses were achieved on a Thermo Flash EA-1112 analyzer.

Scheme 2 – The numbering scheme for NMR assignments in precursors and compounds **1** – **4**.

Synthesis of [2-[(CH₂O)₂CH]C₆H₄]₂Se₂

To a solution of 2-[(CH₂O)₂CH]C₆H₄Br (7 g, 31 mmoli) in 30 mL *n*-hexane, ⁿBuLi (20 mL, 1.6 M, 31 mmoli) in 70 mL *n*-hexane was added dropwise

at room temperature, under inert atmosphere, then the reaction mixture was left stirring for one hour. The secondary product (i.e. *n*-BuBr) was removed via a filtering cannula and then, the organolithium

derivative was washed several times with anhydrous *n*-hexane. The isolated precipitate was dissolved in 100 mL anhydrous THF and selenium powder (2.41 g, 31 mmoli) was added. The reaction mixture was left stirring overnight and the hydrolysis of the obtained lithium selenolate followed by the oxidation were performed. The desired compound was isolated by extraction with CH₂Cl₂, organic layer being dried over anhydrous Na₂SO₄. After filtration, the solvent was removed under reduced pressure yielding the compound as yellow solid. Yield: 5 g (72%). ¹H NMR (400 MHz, CDCl₃): δ = 7.87–7.76 (m, 2H, H-6), 7.54–7.45 (m, 2H, H-3), 7.37–7.21 (m, 4H, H-4,5), 6.04 (s, 2H, H-7), 4.39–3.72 (m, 8H, H-8,9) ppm. ⁷⁷Se{¹H} NMR (76 MHz, CDCl₃): δ = 410 (s) ppm.

Synthesis of [2-(O=CH)C₆H₄]₂Se₂

To a solution of [2-((CH₂O)₂CH)C₆H₄]₂Se₂ (5 g, 31 mmoli) in 50 ml acetone, 1 mL of HCl was added and the reaction mixture was refluxed one hour. The solution was concentrated, 15 mL distilled H₂O was added, and the formed precipitate was isolated by filtration, dissolved in CH₂Cl₂ and dried over anhydrous Na₂SO₄. After filtration, the solvent was evaporated in vacuum and the product was purified by washing it with diethyl ether and *n*-hexane, resulting a pale-yellow solid. Yield: 3.45 g (86%). ¹H NMR (400 MHz, CDCl₃): δ = 10.19 (s, 2H, H-7), 7.88 (m, 2H, H-3,6), 7.43 (m, 4H, H-4,5) ppm. ⁷⁷Se{¹H} NMR (76 MHz, CDCl₃): δ = 456 (s) ppm.

Synthesis of [(Z)-2'-{2-C₆H₅-(4H)-oxazol-5-one}CHC₆H₄]₂Se₂ (1)

[2-(O=CH₂)C₆H₄]₂Se₂ (2) (1.2 g, 3.26 mmoli), *N*-benzoylglycine (1.17 g, 3.52 mmoli) and sodium acetate (1.07 g, 13.04 mmoli) in 2 mL of acetic anhydride were heated to the reflux temperature (100°C) for two hours and then allowed to cool to room temperature. The target compound was precipitated with EtOH as orange solid and was isolated by filtration and washed several times with EtOH. Yield: 1.7 g (80%). M.p. = 227 °C. **Elemental analysis**, calcd. for C₃₂H₂₀N₂O₄Se₂ (MW = 654.46): C, 58.73; H, 3.08; N, 4.28%. Found: C, 58.95; H, 3.07; N, 4.30%. ¹H NMR (400 MHz, CDCl₃): δ = 8.71 (d, ³J_{HH} = 7.8 Hz, 2H, H-3), 8.07 (d, ³J_{HH} = 7.7 Hz, 4H, H-12,16), 7.89 (d, ³J_{HH} = 7.7 Hz, 2H, H-6), 7.63–7.52 (m, 2H, H-7, H-14), 7.45–7.40 (m, 6H, H-13,15), 7.33 (t, 4H, H-4,5) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃): δ = 167.11

(C-9), 163.12 (C-10), 139.03 (C-1), 136.32 (C-4), 135.37 (C-7), 133.99 (C-6), 133.53 (C-13), 132.84 (C-2), 131.69 (C-5), 130.44 (C-8), 129.88 (C-12,16), 129.03 (C-14), 128.07 (C-13,15), 125.54 (C-11) ppm. ⁷⁷Se{¹H} NMR (76 MHz, CDCl₃): δ = 475 (s) ppm. **HRMS** (APCI+, MeOH), m/z (%): 327.99713 (100), [C₁₆H₁₀NO₂Se]⁺, calcd. for C₁₆H₁₀NO₂Se: m/z = 328.06667. **IR** (KBr pellet, ν, cm⁻¹): 1796 (s)/1769 (w) [ν(C=O)], 1647 (m) [ν(C=N)], 1573 (m), 1551 (m), 1487 (w), 1447 (w), 1428 (w), 1357 (w), 1324 (w), 1292 (w), 1220 (w), 1161 (s) [ν(C-O)], 1106 (m), 1068 (w), 1026 (w), 975 (w), 856 (m), 765 (w), 699 (m), 667 (m).

Synthesis of [ZnCl₂{[(Z)-2'-{2-C₆H₅-(4H)-oxazol-5-one}CHC₆H₄]₂Se₂}] (2)

To a clear solution of **1** (0.2 g, 0.31 mmoli) in 20 mL THF, ZnCl₂ (0.04 g, 0.31 mmoli) was added. After one hour of stirring, the solvent was removed in vacuum and the yellow solid was washed with *n*-hexane (3 x 10 mL). Yield: 0.230 (96%). M.p: 224°C. **Elemental analysis**, calcd. for C₃₂Cl₂H₂₀N₂O₄Se₂Zn (MW = 790.74): C, 48.61; H, 2.55; N, 3.54%. Found: C, 49.06; H, 3.46; N, 3.51%. ¹H NMR (400 MHz, CDCl₃): δ = 8.70 (dd, *J* = 7.9 Hz, 2H, H-3), 8.07 (d, ³J_{HH} = 7.7 Hz, 4H, H-12,16), 7.90 (d, ³J_{HH} = 7.7 Hz, 2H, H-6), 7.55–7.52 (m, 4H, H-7, H-14), 7.45–7.39 (m, 6H, H-4,13,15), 7.32 (t, *J* = 7.6 Hz, 2H, H-5) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃): δ = 166.03 (C-9), 164.43 (C-10), 137.02 (C-1), 136.42 (C-4), 135.43 (C-7), 134.419 (C-6), 133.29 (C-13), 132.47 (C-2), 131.14 (C-5), 129.80 (C-8), 128.85 (C-12,16), 128.55 (C-14), 128.11 (C-13,15), 125.42 (C-11) ppm. ⁷⁷Se{¹H} NMR (76 MHz, CDCl₃): δ = 476 (s) ppm. **HRMS** (ESI+, MeCN), m/z (%): 719.06111 (10), [M-Cl₂]⁺, calcd. for C₁₆H₁₀NO₂Se: m/z = 719.90395. **IR** (KBr pellet, ν, cm⁻¹): 1796 (s)/1767 (w) [ν(C=O)], 1646 (m) [ν(C=N)], 1550 (m), 1485 (m), 1446 (w), 1357(w), 1324 (w), 1292 (w), 1220 (w), 1161 (s) [ν(C-O)], 1105 (w), 1068 (w), 975 (w), 887 (m), 764 (w), 698 (m). *A*_m = 0.45 Ω⁻¹·cm²·mol⁻¹.

Synthesis of [CdCl₂{[(Z)-2'-{2-C₆H₅-(4H)-oxazol-5-one}CHC₆H₄]₂Se₂}] (3)

CdCl₂ (0.056 g, 0.31 mmoli) was added to a clear solution of **1** (0.2 g, 0.31 mmoli) in 20 mL THF. After one hour of stirring, the solvent was removed in vacuum and the yellow solid was washed with *n*-hexane (3 x 10 mL). Yield: 0.248 (97%). M.p: 222°C. **Elemental analysis**, calcd. for C₃₂Cl₂H₂₀N₂O₄Se₂Cd (MW = 837.78): C, 45.88; H, 2.41; N, 3.34%. Found: C, 45.07; H, 2.37; N, 3.10%.

$^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 8.71$ (d, $J = 8.0$ Hz, 2H, H-3), 8.07 (d, $J = 7.6$ Hz 4H, H-12,16), 7.89 (d, $J = 7.8$ Hz, 2H, H-6), 7.59–7.52 (m, 4H, H-7,14), 7.46–7.40 (m, 6H, H-5,13,15), 7.33 (t, $J = 7.5$ Hz, 2H, H-4) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): $\delta = 167.66$ (C-9), 164.79 (C-10), 137.66 (C-1), 136.32(C-4), 135.36 (C-7), 133.99 (C-6), 133.53 (C-13), 132.84 (C-2), 131.69 (C-5), 130.43 (C-8), 129.88 (C-14), 129.02 (C-12,16), 128.52 (C-13,15), 125.53 (C-11) ppm. $^{77}\text{Se}\{^1\text{H}\}$ NMR (76 MHz, CDCl_3): $\delta = 476$ (s) ppm. IR (KBr pellet, ν , cm^{-1}): 1796 (s)/1769 (w) [$\nu(\text{C}=\text{O})$], 1647 (m) [$\nu(\text{C}=\text{N})$], 1573 (w), 1551 (m), 1487 (w), 1447 (w), 1428 (w), 1357 (w), 1324 (w), 1292 (w), 1220 (w), 1161 (s) [$\nu(\text{C}-\text{O})$], 1106 (m), 1026 (w), 975 (w), 856 (m), 765 (w), 699 (m). $A_m = 0.93 \Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$.

Synthesis of $[\text{HgCl}_2\{[(Z)\text{-}2'\text{-}\{2\text{-C}_6\text{H}_5\text{-}(4H)\text{-oxazol-5-one}\}\text{CHC}_6\text{H}_4\}_2\text{Se}_2\}]$ (**4**)

To a solution of **1** (0.2 g, 0.31 mmol) in 20 mL THF, HgCl_2 (0.08 g, 0.31 mmol) was added and after one hour of stirring, the solvent was removed in vacuum and the yellow solid was washed with *n*-hexane (3×10 mL). Yield: 0.251 (90%). M.p: 218°C. **Elemental analysis**, calcd. for $\text{C}_{32}\text{Cl}_2\text{H}_{20}\text{N}_2\text{O}_4\text{Se}_2\text{Hg}$ (MW = 925.96): C, 41.51; H,

2.18; N, 3.03%. Found: C, 51.25; H, 2.18; N, 3.01%. $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 8.71$ (dd, $J = 7.9$, 1.6 Hz, 2H, H-3), 8.08 – 8.05 (m, 4H, H-12,16), 7.89 (dd, $J = 7.7$, 1.4 Hz, 2H, H-6), 7.59–7.52 (m, 4H, H-7,14), 7.46–7.40 (m, 6H, H-5,13,15), 7.33 (td, $J = 7.5$, 1.6 Hz, 2H, H-4) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): $\delta = 167.11$ (C-9), 164.87 (C-10), 139.60 (C-1), 136.32 (C-4), 135.37 (C-7), 133.99 (C-6), 133.53 (C-3), 132.84 (C-2), 131.69 (C-5), 130.43 (C-8), 129.88 (C14), 129.02 (C-12,16), 128.52 (C-13,15), 125.06 (C-11) ppm. $^{77}\text{Se}\{^1\text{H}\}$ NMR (76 MHz, CDCl_3): $\delta = 476$ (s) ppm. IR (KBr pellet, ν , cm^{-1}): 1796 (s)/1769 (w) [$\nu(\text{C}=\text{O})$], 1647 (s) [$\nu(\text{C}=\text{N})$], 1583 (m), 1573 (m), 1552 (w), 1488 (w), 1447 (w), 1428 (w), 1358 (m), 1324 (w), 1293 (w), 1221 (w), 1161 (s) [$\nu(\text{C}-\text{O})$], 1106 (w), 1068 (w), 1026 (w), 976 (w), 929 (w), 8876 (m), 765 (m), 699 (m), 667 (m). $A_m = 2.61 \Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$.

Crystal structure determination

A suitable crystal of **1** was mounted on MiTeGen microMounts cryoloops and data were collected on a Bruker D8 VENTURE diffractometer using Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) from an $\text{I}\mu\text{S}$ 3.0 microfocus source with multilayer optics, at low temperature (100 K).

Table 3

Crystal data and structure refinement for compound **1**

| | | |
|--|--|---------------------|
| Empirical formula | $\text{C}_{32}\text{H}_{20}\text{N}_2\text{O}_4\text{Se}_2$ | |
| Formula weight | 654.24 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 \AA | |
| Crystal system | monoclinic | |
| Space group | $P2_1/c$ | |
| Unit cell dimensions | $a = 11.7455(3) \text{ \AA}$ | $\alpha = 90^\circ$ |
| $b = 19.4668(6) \text{ \AA}$ | $\beta = 112.9920(10)^\circ$ | |
| $c = 12.2127(3) \text{ \AA}$ | $\gamma = 90^\circ$ | |
| Volume | $2570.57(12) \text{ \AA}^3$ | |
| Z | 4 | |
| Density (calculated) | 1.691 Mg/m^3 | |
| Absorption coefficient | 2.921 mm^{-1} | |
| $F(000)$ | 1304 | |
| Crystal size | $0.198 \times 0.212 \times 0.251 \text{ mm}^3$ | |
| Theta range for data collection | 2.09 to 28.31° | |
| Index ranges | $-15 \leq h \leq 15$, $-25 \leq k \leq 25$, $-16 \leq l \leq 16$ | |
| Reflections collected | 57597 | |
| Independent reflections | 6397 [R(int) = 0.0382] | |
| Completeness to $\theta = 28.31^\circ$ | 99.9% | |
| Refinement method | Full-matrix least-squares on F^2 | |
| Data / restraints / parameters | 6397 / 0 / 361 | |
| Goodness-of-fit on F^2 | 1.031 | |
| Final R indices [I > 2 σ (I)] | $R1 = 0.0225$, $wR2 = 0.0516$ | |
| R indices (all data) | $R1 = 0.0293$, $wR2 = 0.0545$ | |
| Largest diff. peak and hole | 0.366 and $-0.321 \text{ e.\AA}^{-3}$ | |

For structure solving and refinement, the Bruker APEX3 Software Package was used.²³ 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.²⁴ Intermolecular contacts were found in Platon.²⁵ Table 3 contain the details of the crystal structure determination and refinement.

CONCLUSIONS

The similar chemical shifts of the proligand **1** ($\delta = 475$ ppm) and its metal complexes **2–4** ($\delta = 476$ ppm) suggest that Se–M (M = Zn, Cd, and Hg) interactions are likely absent in solution, with metal coordination occurring only through the nitrogen atoms from the oxazolone rings.

[(*Z*)-2'-{2-C₆H₅-(4*H*)-oxazol-5-one}CHC₆H₄]₂Se₂ (**1**) exhibited strong absorption band characterized by large molar extinction coefficients, assigned to the electron donor properties of the 2-C₆H₅-(4*H*)-oxazol-5-one rings in the UV-Vis spectra, with no modification in the intensity of the bands for the metal complexes.

The single-crystal X-ray diffraction studies revealed the formation of a supramolecular 3D architecture in **1**, obtained by CH \cdots O contacts between pair of dimers held together by $\pi\cdots\pi$ contacts.

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Supplementary material

CCDC 2422717 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.

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