

*Dedicated to Professor Ion Grosu  
on the occasion of his 65th anniversary*

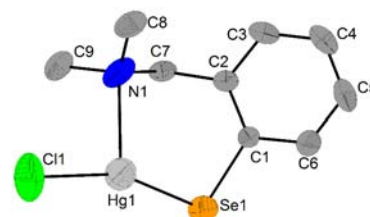
## SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF MERCURY(II) METAL COMPLEXES CONTAINING THE 2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>Se LIGAND

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The heteroleptic mercury(II) complex [HgCl<sub>2</sub>{SeC<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>NMe<sub>2</sub>)-2}] (**1**) was prepared by reacting the corresponding lithium organoselenolate in an equimolar ratio with HgCl<sub>2</sub>. The complex [Hg(SCN){SeC<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>NMe<sub>2</sub>)-2}] (**2**) was prepared by the salt metathesis reaction between **1** and KSCN in a 1:1 molar ratio. The metal complexes were characterized in solution by multinuclear NMR spectroscopy and mass spectrometry and the solid state structure of **1** was determined by single crystal X-ray diffraction. In the crystal of **1** a 1D zig-zag polymeric chain was formed by Se...Hg secondary interactions.



### INTRODUCTION

Group 12 metal complexes are of current attention in the scientific community due to their structural features and their potential applications in the field of nanomaterials and opto-electronics.<sup>1-4</sup> Metal complexes heaving organoselenolato (RSe<sup>-</sup>) ligands containing additional donor (nitrogen, oxygen, chalcogen) atoms in the organic group attached to the selenium atom are valuable candidates as precursors for metal selenides,<sup>5-8</sup> the stability of metal selenolates being significantly increased by chelation. On the other hand, various compounds with chalcogen donor atoms were studied as efficient ligands for mercury complexation, in order to develop new systems for the removal of heavy metals, either from environment or living organisms.<sup>9</sup> Potentially multidentate ligands can constrain the geometric environments

associated with the metal binding and were established as useful tools for the preparation of mononuclear complexes for further applications, *i.e.* 2-(4,4-dimethyloxazolino)benzeneselenolate and 2-phenyl-*N,N*-diisopropylbenzamide ligands were successfully used to obtain monomeric mercury(II) complexes and insights of the coordination behaviour of such ligands to mercury were well documented.<sup>10-11</sup>

We have previously developed heteroleptic organoselenium ligands containing a nitrogen and a selenium heteroatoms, and we have explored their coordination chemistry with group 12,<sup>12</sup> with coinage metals,<sup>13</sup> and with tetrelenes.<sup>14</sup> Several homoleptic zinc and cadmium complexes of type (RSe)<sub>2</sub>M [R = 2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>; M = Zn, Cd] were prepared and the main features of their coordination chemistry were established.<sup>15</sup> As a continuation of this line of research, we are now

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reporting on the preparation and structural characterization of new mercury stable species, using [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>Se] moiety, capable for intramolecular coordination.

## RESULTS

Two new mercury(II) metal complexes were isolated as air-stable yellow solids. NMR spectroscopy, mass spectrometry and X-ray diffraction in case of compound **1**, were employed to elucidate the structures of the mercury complexes.

[HgCl{SeC<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>NMe<sub>2</sub>)-2}] (**1**) has been prepared by the salt metathesis reaction between HgCl<sub>2</sub> and one equivalent of the corresponding lithium organoselenolate, previously obtained by *ortho*-lithiation of *N,N*-dimethylbenzylamine and insertion of elemental selenium into to the new formed C–Li bond (Scheme 1).

Recrystallization of **1** from a mixture of dichloromethane and *n*-hexane allowed the formation of yellow crystals suitable for X-ray diffraction.

The complex [Hg(SCN){SeC<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>NMe<sub>2</sub>)-2}] (**2**) was prepared by KCl elimination in the reaction of [HgCl{SeC<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>NMe<sub>2</sub>)-2}] (**1**) and KSCN, in a 1:1 molar ratio, as depicted in Scheme 1.

Mass spectra are consistent with the expected formulas, the base peak being the molecular ion of the complexes (*m/z* 451.95844 for **1** and *m/z* 474.96654 for **2**).

## DISCUSSION

### Spectroscopic characterization

The room temperature <sup>1</sup>H and <sup>13</sup>C NMR spectra in CDCl<sub>3</sub> solution confirm the proposed structures for the two complexes and display for both of them a similar pattern of the resonances determined by the organic group bonded to mercury. The <sup>1</sup>H NMR spectra of the complexes present one set of sharp singlet resonances in the aliphatic region corresponding to the methyl and methylene moieties in the pendant arm of the organic group attached to the selenium atom and multiplet resonances in the aromatic region. In the <sup>13</sup>C NMR spectra of the complexes all the expected resonances were observed.

The <sup>77</sup>Se NMR spectra of the complexes reveal one singlet resonance, in complex **2** at δ 47 ppm, high field shifted when compared to complex **1** (δ 67 ppm) and low field shifted compared with the homoleptic mercury organoselenolate containing [2-[1-(3,5-dimethylphenyl)-2-naphthyl]-4,5-dihydro-4,4-dimethyloxazole] group (δ = 4 ppm).<sup>16</sup>

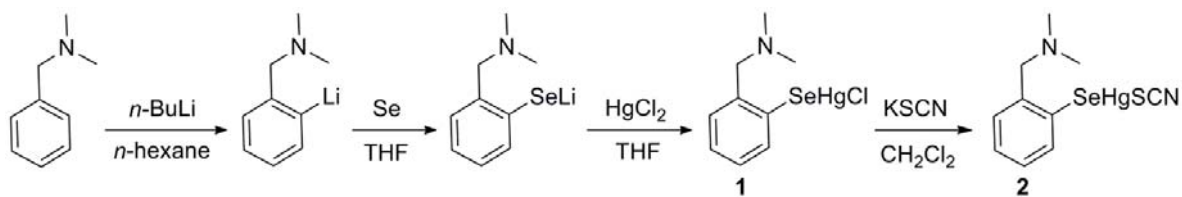
In the <sup>119</sup>Hg NMR spectrum of **1**, one broad singlet resonance was observed at δ = -1290 ppm. Unfortunately, for complex **2** the <sup>119</sup>Hg NMR resonance was not observed.

The ESI+ HRMS spectra of both metal complexes displayed the pseudo-molecular peak [M+H]<sup>+</sup> as a base peak, at *m/z* 451.95844 for complex **1** and *m/z* 474.96457 for complex **2**. In complex **2** a peak corresponding to the [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>Se]<sup>+</sup> was observed also, at *m/z* 214.01207.

### Crystal and molecular structure of [HgCl{SeC<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>NMe<sub>2</sub>)-2}]

Slow diffusion of *n*-hexane into a dichloromethane solution of **1** allowed the formation of single crystals appropriate for X-ray diffraction. The molecular structure of **1** is shown in Figure 1 and selected interatomic distances and angles are listed in Table 1.

As observed previously for other metal complexes containing the 2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>Se ligand,<sup>7,15,17</sup> in solid state the nitrogen atom in the pendant arm is strongly coordinated to the metal center and not to the selenium atom, as in the diorganodiselenide or the diorganoselenide.<sup>18</sup> The N→Hg interaction of 2.4838(7) Å (cf. Σ<sub>r<sub>vdw</sub></sub>(N,Hg) 3.04 Å<sup>19</sup>) in **1** is stronger than the N→Hg interactions found for [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]HgX, (X = halide, dithiocarbamate ligand)<sup>20</sup> or [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>Se]<sub>2</sub>Hg,<sup>4</sup> which are in the range 2.64 – 2.71 Å. The intramolecular coordination of nitrogen results in a *N,Se*-bidentate, chelating, behaviour of the ligand and a trigonal pyramidal environment around the mercury atom (Hg is out from the Se1/N1/C11 plane at 0.26 Å). In this way a non-planar six-membered C<sub>3</sub>SeNHg ring is formed, having a distorted boat conformation, with Se1 and C7 in apices. The Se–Hg bond length (Hg(1)–Se(1) 2.4646(7) Å; cf. Σ<sub>r<sub>vdw</sub></sub>(N,Hg) 3.50 Å<sup>19</sup>) is similar to those found in MeHg(SeC<sub>6</sub>H<sub>2</sub>Pr<sup>*i*</sup><sub>3</sub>-2,4,6),<sup>21</sup> and Hg(Se-2-NC<sub>5</sub>H<sub>4</sub>)<sub>2</sub> (2.460 Å and 2.458 Å, respectively).<sup>22</sup>



Scheme 1

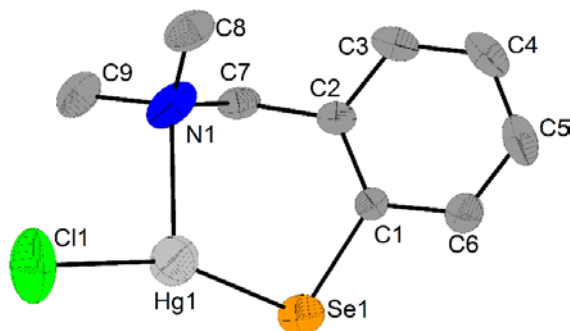
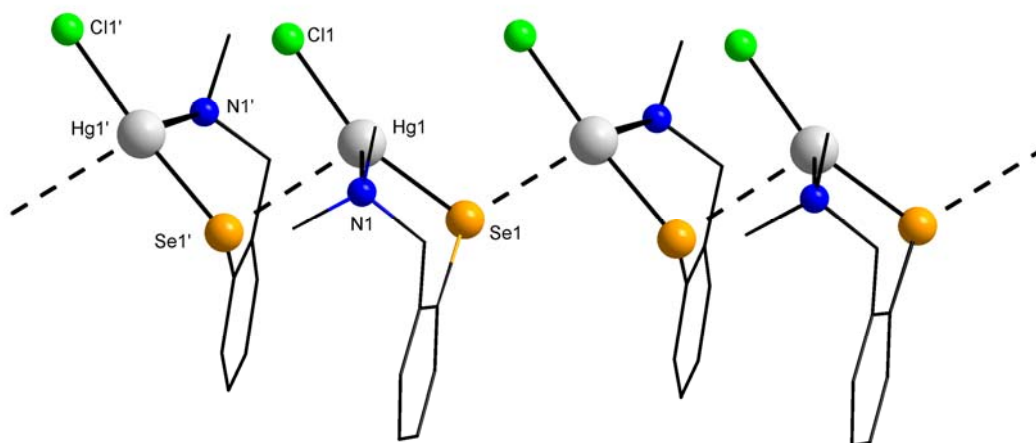
Fig. 1 – Ellipsoid representation of **1**. Thermal ellipsoids are drawn with 50% probability. Hydrogen atoms were omitted for clarity.

Table 1

Selected bond distances [Å] and angles [°] for compound **1**<sup>a</sup>

Hg1–Se1	2.4646(7)	Se1–Hg1–Cl1	157.94
Hg1–Cl1	2.3603(7)	Se1–Hg1–N1	94.81
Hg1–N1	2.4838(7)	Se1–Hg1–Se1'	104.63
		Cl1–Hg1–N1	101.88
Hg1–Se1'	3.0998(9)	Cl1–Hg1–Se1'	89.16
		N1–Hg1–Se1'	92.23
		Hg1–Se1–C1	96.65
		Hg1–Se1–Hg1'	100.53
		Cl1–Se1–Hg1'	111.49

<sup>a</sup> Symmetry equivalent position  $-\frac{1}{2} + x, \frac{1}{2} - y, z$  is given by 'prime'Fig. 2 – View along *c* axis of the 1D polymeric chain in the crystal of **1**.

The Hg1–Cl1 bond length (2.3603(7) Å) is similar to those found in dichloro-(bis(2-(4,4-dimethyl-1,3-oxazolin-2-yl)phenyl)selenide)-mercury(II) (2.394 Å and 2.398 Å)<sup>23</sup> and shorter

than that found in cyclo-tetrakis(chloro-( $\mu^2$ -ethane-selenolato-pyridine-mercury(II) (2.546 Å).<sup>24</sup>

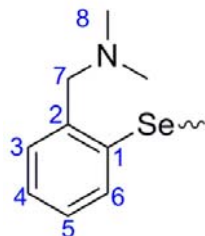
Additional Se···Hg secondary interactions between neighbouring molecules give rise to a zig-

zag 1D polymeric chain, disclosing four-coordinate mercury atoms with a distorted *seesaw* arrangement and three-coordinate selenium atoms (Figure 2). Se1...Hg1 interactions of 3.0998(9) Å are in the range found in [(PhSe)<sub>7</sub>Hg<sub>4</sub>(SCN)Py]<sub>n</sub> (2.5486(13) - 3.438(1) Å).<sup>25</sup> No further interactions were observed in the crystal.

## EXPERIMENTAL

### General experimental information

The starting materials (*n*-BuLi, Se, HgCl<sub>2</sub>, KSCN) were commercially available from Sigma Aldrich and used without additional purification. The solvents used for the preparation of the metal complexes were dried and distilled under argon following standard techniques. Melting points were measured on an Electrothermal 9200 apparatus. HRMS ESI+ mass spectra were recorded using a Thermo Scientific LTQ-OrbitrapXL instrument equipped with a standard ESI/APCI source. Multinuclear NMR spectra were recorded at room temperature in dry CDCl<sub>3</sub>, on a BRUKER AVANCE 400 instrument operating at 400.13, 100.61, 71.66 and 76.31 MHz for <sup>1</sup>H, <sup>13</sup>C, <sup>199</sup>Hg and <sup>77</sup>Se, respectively. The <sup>1</sup>H and <sup>13</sup>C chemical shifts are reported in ppm relative to the residual peak of the solvent (ref. CHCl<sub>3</sub>: <sup>1</sup>H 7.26, <sup>13</sup>C 77.0 ppm). 2D NMR experiments (COSY, HMQC and HMBC) were employed to assign the <sup>1</sup>H and <sup>13</sup>C resonances according to the numbering shown in Scheme 2. The NMR spectra were processed using the MestReNova software.<sup>26</sup>



Scheme 2

### Synthesis of [HgCl{SeC<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>NMe<sub>2</sub>)-2}] (1)

To a stirred solution of *N,N*-dimethylbenzylamine (0.267 g, 1.98 mmol) in 40 mL *n*-hexane was added dropwise a solution of *n*-BuLi (1.24 mL, 1.6 M, 1.98 mmol) in *n*-hexane, at r.t., under argon atmosphere and the reaction mixture was refluxed for 3 h. After cooling the mixture to room temperature, the solvent was evaporated *in vacuo* to yield the lithium derivative as a colorless solid. The lithium intermediate was dissolved in 40 mL THF, elemental selenium (0.156 g, 1.98 mmol) was added and the reaction mixture was stirred for 2 h. To the resulting solution an equivalent of HgCl<sub>2</sub> (0.539 g, 1.98 mmol) was added and the reaction mixture was stirred at room temperature for 24 h. After evaporating *in vacuo* the solvent, dichloromethane was added to the formed precipitate. LiCl was removed by filtration, the solvent was evaporated and the solid was washed with *n*-pentane to yield a yellow solid. Yield 0.594 g, 67 %. M.p. 128°C. <sup>1</sup>H NMR, δ (ppm): 7.71 (d, <sup>3</sup>J<sub>HH</sub> = 7.45 Hz, 1H, H-6), 7.15 – 7.24 (m, 2H, H-4, H-5), 7.11 (d, <sup>3</sup>J<sub>HH</sub> = 6.96 Hz, 1H, H-3), 3.77 (s, 2H, H-7), 2.28 (s, 6H, H-

8). <sup>13</sup>C NMR, δ (ppm): 137.73 (C-1), 137.18 (C-6), 132.92 (C-3), 129.32 (C-5), 128.09 (C-2), 127.78 (C-4), 65.63 (C-7), 45.18 (C-8). <sup>77</sup>Se NMR, δ (ppm): 67. <sup>199</sup>Hg NMR, δ (ppm): -1290. HRMS (ESI+), *m/z* (%): 451.95844 (100), [M+H]<sup>+</sup> calcd. for C<sub>9</sub>H<sub>12</sub>NSeHgCl: *m/z* = 451.96025.

### Synthesis of [Hg(SCN){SeC<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>NMe<sub>2</sub>)-2}] (2)

A mixture of KSCN (0.022 g, 0.22 mmol) and compound **1** (0.1 g, 0.22 mmol) in dichloromethane was stirred for 24 h at room temperature. The formed colourless precipitate was filtrated, the solvent was evaporated and the solid was washed with *n*-hexane to yield the title compound as a yellow solid. Yield: 0.089 g, 85 %. M.p. 95°C. <sup>1</sup>H NMR, δ (ppm): 7.73 (d, <sup>3</sup>J<sub>HH</sub> = 7.22 Hz, 1H, H-6), 7.14 – 7.27 (m, 3H, H-3, H-4, H-5), 3.81 (s, 2H, H-7), 2.36 (s, 6H, H-8). <sup>13</sup>C NMR, δ (ppm): 137.36 (C-1), 137.15 (C-6), 133.11 (C-3), 129.59 (C-5), 128.36 (C-2), 127.92 (C-4), 119.4 (SCN), 65.99 (C-7), 46.06 (C-8). <sup>77</sup>Se NMR, δ (ppm): 47. HRMS (ESI+), *m/z* (%): 474.96457 (100), [M+H]<sup>+</sup>; *m/z* (%): 214.01207 (60), [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>Se]<sup>+</sup> calcd. for C<sub>10</sub>H<sub>12</sub>N<sub>2</sub>SeHgS: *m/z* = 474.96654 and for C<sub>9</sub>H<sub>12</sub>NSeH: *m/z* = 214.01295.

### Crystal structure determination

The details of the crystal structure determination and refinement for compound **1** are given in Table 2. Data were collected on a Bruker SMART APEX diffractometer by using a graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The crystal was attached with epoxy glue on cryoloops and the data were collected at room temperature (297 K). The structure was refined with anisotropic thermal parameters. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement the software package SHELX-2014 was used.<sup>27</sup> The drawings were created with the Diamond program.<sup>28</sup> Crystal data and structure refinement for compound **1** are shown in Table 2.

## CONCLUSIONS

Two new heteroleptic mercury(II) complexes containing the organoselenolato ligand 2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>Se were prepared and structurally characterized in solution by multinuclear NMR spectroscopy and mass spectrometry. The molecular structure of **1** was determined by single crystal X-ray diffraction.

One set of sharp singlet resonances in the <sup>1</sup>H NMR spectra assigned to the methyl and methylene protons in the pendant arm of the 2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>Se fragment, suggested no intramolecular interactions in solution.

Strong intramolecular N→Hg coordination and the formation of a 1D *zig-zag* polymeric chain, formed by Se...Hg secondary interactions were observed in the crystal structure of **1**, where the organoselenolato ligand behaves as a Se<sub>2</sub>N-bidentate triconnectiv moiety.

Table 2  
Crystal data and structure refinement for compound 1

Empirical formula	C <sub>9</sub> H <sub>12</sub> ClHgNSe	
Formula weight	449.20	
Temperature	294(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pna21	
Unit cell dimensions	a = 8.552(2) Å b = 13.650(4) Å c = 10.044(3) Å	α = 90° β = 90° γ = 90°
Volume	1172.6(5) Å <sup>3</sup>	
Z	4	
Density (calculated)	2.544 Mg/m <sup>3</sup>	
Absorption coefficient	16.414 mm <sup>-1</sup>	
F(000)	816	
Crystal size	0.310 x 0.280 x 0.230 mm <sup>3</sup>	
Theta range for data collection	2.518 to 24.993°	
Index ranges	-10 ≤ h ≤ 10, -16 ≤ k ≤ 16, -11 ≤ l ≤ 11	
Reflections collected	10625	
Independent reflections	2068 [R(int) = 0.0353]	
Completeness to theta = 24.993°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1 and 0.080	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	2068 / 1 / 120	
Goodness-of-fit on F <sup>2</sup>	1.027	
Final R indices [I > 2σ(I)]	R1 = 0.0231, wR2 = 0.0504	
R indices (all data)	R1 = 0.0266, wR2 = 0.0520	
Absolute structure parameter	-0.005(8)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.639 and -0.603 e.Å <sup>-3</sup>	

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### Supplementary material

CCDC 1963489 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).

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