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New N,Se-Chelate Ligand
2-Phenylselenomethyl-1H-benzimidazole:
Electrochemistry and Structure**

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**Silver(I), Copper(I) and Copper(II) Complex of the New
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benzimidazole: Electrochemistry and Structure**

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Keywords:	Copper compounds, Crystal structures, Electrochemistry, Selenoether ligand, Silver complex



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3 **Silver(I), Copper(I) and Copper(II) Complex of the New N,Se-Chelate**
4
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6 **Ligand 2-Phenylselenomethyl-1*H*-benzimidazole: Electrochemistry and**
7
8
9 **Structure**
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13 **Markus Leboschka,^[a] Monika Sieger,^[a] Biprajit Sarkar,^[a] Mark Niemeyer,^[b] Thilo**
14
15 **Schurr,^[a] Jan Fiedler,^[c] Stanislav Zális,^[c] Wolfgang Kaim ***
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21 Stuttgart, Institut für Anorganische Chemie der Universität Stuttgart
22

23 Received
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25
26 *Dedicated to Professor Gerd Meyer on the Occasion of his 60th Birthday*
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32

33 **Abstract.** 2-Phenylselenomethyl-1*H*-benzimidazole (psbi) can form complexes in 2:1 ratio
34
35 with coinage metal ions. Crystal structure analysis revealed a flattened metal coordination for
36
37 $[\text{Ag}^{\text{I}}(\text{psbi})_2](\text{BF}_4)$ (**1**), approaching a distorted planar arrangement with weak Ag-Se bonds (d
38
39 > 2.9 Å) and confirmed as energy minimum by DFT calculations. The typical Jahn-Teller
40
41 system $[\text{Cu}^{\text{II}}(\text{psbi})_2\text{Cl}_2]$ (**2**) exhibits a planar CuN_2Cl_2 core with weak Se---Cu---Se axial
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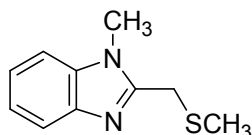
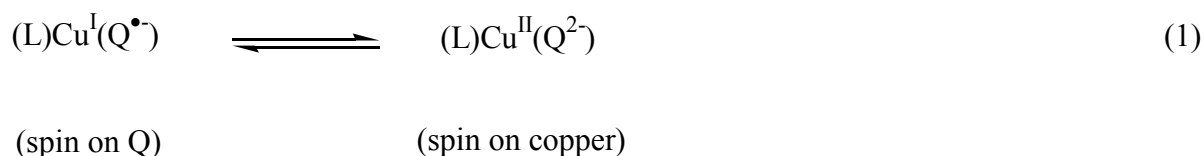
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3 ligation (3.2944(8) Å Cu--Se distance). The oxygen-sensitive compound [Cu^I(psbi)₂](BF₄) (**3**)
4
5 exhibits electrochemically reversible oxidation in contrast to the silver(I) analogue **1**.
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10 **Keywords:** Copper compounds; Crystal structures; Electrochemistry; Selenoether ligand;
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12 Silver complex
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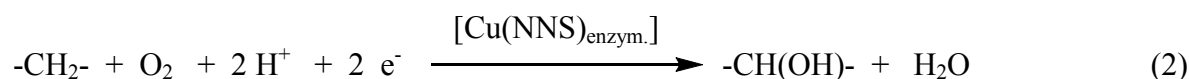
17 **Introduction**

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22 Organoselenium ligands have found increasing attention in coordination chemistry [1,2], not
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24 in the least due to the biological role of this element [3,4]. Although the increasingly used
25
26 selenomethionine [5] does not play the same important biological role as the easily
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28 deprotonated selenocysteine (the "21st essential amino acid" [4]), selenoether donors are
29
30 being employed as probes for NMR spectroscopic and X-ray crystallographic investigations
31
32 of biomolecules [5a]. Following recent work on copper(I), silver(I) and copper(II) complexes
33
34 of small mixed imine-N and thioether-S chelate ligands such as 1-methyl-2-
35
36 (methylthiomethyl)-*IH*-benzimidazole (mmb) [6-9] we have started to extend this approach to
37
38 related imine-N/selenoether-Se species [10]. The mmb ligand did not only allow us to observe
39
40 [9] the biochemically relevant [11] valence-tautomer equilibrium (1) outside an enzyme, it
41
42 also showed a remarkable ability to allow for facile Cu^{II} transitions [6,12] because of very
43
44 unusual complex geometries [6] as illustrated by a "see-saw" configuration [13] around the
45
46 metal in [Cu(mmb)₂]⁺ with its 2+2 coordination arrangement [6]. The analogous ion
47
48 [Ag(mmb)₂]⁺ showed a much less distorted tetrahedral arrangement than the copper(I)
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50 complex due to comparatively enhanced M-S bonding [8].
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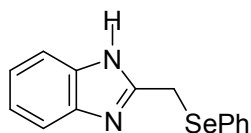
mmb

Due to the electrochemically reversible electron transfer [6] such systems are not only a minimal model for partially S-ligand coordinated copper electron transfer centers of type 1 in “blue copper proteins” [14], they have also become interesting for attempts [15] to mimic and understand the role of mixed histidine/methionine coordinated copper in substrate selective monooxygenases such as PHM (peptidylglycine hydroxylating monooxygenase) [16] which use intermediately coordinated O_2 to convert activated CH_2 groups to CHOH functions (2).



In addition to the biochemical context related to the function of thioethers [17], molecular copper complexes of sulfur or selenium containing ligands [2] may be of interest as potential precursor components for obtaining copper/indium/gallium/selenide or -sulfide (CIGS) photovoltaic materials CuME_2 ($\text{M} = \text{In}, \text{Ga}$; $\text{E} = \text{S}, \text{Se}$) [18].

We now report a selenium-containing ligand related to mmb, viz., 2-phenylselenomethyl-*1H*-benzimidazole (psbi), and the structures of its silver(I) and copper(II) complexes **1** and **2**. The copper(I) compound **3**, analogous to **1** and related to **4**, and its electrochemical response are also described (Scheme 1).



psbi

Due to the rather different structural results found for the selenium-containing complex **1** and the previously reported [8] sulfur analogue **5** within the four-coordination regime [13] we undertook a DFT study of that structurally puzzling ion $[\text{Ag}(\text{psbi})_2]^+$ in order to confirm the experimental result.

Scheme 1

$[\text{Ag}(\text{psbi})_2](\text{BF}_4)$	1
$[\text{Cu}(\text{psbi})_2\text{Cl}_2]$	2
$[\text{Cu}(\text{psbi})_2](\text{BF}_4)$	3
$[\text{Cu}(\text{mmb})_2](\text{BF}_4)$	4
$[\text{Ag}(\text{mmb})_2](\text{PF}_6)$	5

The bonding of thioether and selenoether functions to transition metals has been reviewed and discussed with respect to possible π acceptor effects [1a,19,20], while recent results of methionine-rich copper(I) metalloproteins with regulatory and other functions [17] also stimulate studies in the field.

Results and Discussion

Synthesis, Characterization, and Crystallization

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3 The bidentate psbi ligand, offering a benzimidazole imino function and an
4 arylalkylselenoether donor, was obtained in a straightforward way. The arylseleno function is
5 helpful for obtaining mononuclear complexes, the analogous dialkylselenoether ligand 2-
6 methylselenomethyl-*IH*-benzimidazole gave a disilver(I) species with an Ag--Ag distance of
7
8 3.156(1) Å [10].
9

10 The new crystalline materials **1** and **2** were analyzed by X-ray diffraction, Figures 1-3
11 illustrate the molecular and crystal structures and the Tables 1-3 summarize the
12 crystallographic data and structure parameters.
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Tables 1-3

Figures 1-3

The two new structures do not show unusual intermolecular interactions. Hydrogen bonding
NH---F from the benzimidazole-NH to the counter ions (**1**: 2.837(8) Å for N4(H)---F3(BF₄)
as shortest such distance) and rather marginal [19,21] intermolecular Se---Se contacts at $d \geq$
4.0 Å can be noted. The molecules of the copper(II) complex **2** arrange in a corrugated plane
structure (Figure 3) with significant [22] intermolecular N(H)---Cl(Cu) interactions at
3.1706(6) Å. Although no pronounced π - π stacking could be found, the arrangement of the
aromatic benzimidazole and phenyl π systems is noteworthy. In all two cases the metal-
connected benzimidazoles are approximately coplanar with the phenyl rings from the
CH₂SePh substituents either above and below (**2**) or both above (**1**) that plane.

Concerning the molecular structures, the silver(I) compound **1** shows a rather distorted
arrangement, approaching a square configuration. The copper(II) species **2** exhibits a planar
CuN₂Cl₂ core with weak Se---Cu^{II}---Se axial ligation at 3.2944(8) Å Cu-Se distance,

The M-N bond lengths show only a slight variation on replacement of mmb by the
selenium-containing ligand psbi but a large difference of about 0.32 Å on going from Cu⁺ (**4**)

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2
3 to Ag⁺ (**1,5**), reflecting the difference (1.26 Å - 0.96 Å) of the ionic radii [22]. On the other
4
5 hand, the copper(II)-N(imine) bond in **2** is typically longer than the copper(I)-N(imine) bond
6
7 in **4** as a consequence of absent π back donation. The M-E distances (E = S or Se) show
8
9 substantial increase between the complexes of Cu⁺ (**4**) or Ag⁺ (**1,5**) and mmb (**4,5**) or psbi
10
11 ligands (**1**). Remarkably, the cations in the crystal of [Ag(psbi)₂](BF₄) exhibit two quite
12
13 different Ag-Se distances at 2.923(1) and 3.040(1) Å, indicating structural flexibility of this
14
15 weak bonding (shallow energy surface); the sum of the van der Waals radii of Se and Ag is
16
17 about 3.60 Å [22]. The difference to the Ag-S distance of 2.7019(8) Å in **5** [8] is striking. The
18
19 still longer Cu^{II}---Se distance in **2** corresponding to the sum of the van der Waals radii at 3.30
20
21 Å [22] illustrates the familiar tetragonal stretching of a Jahn-Teller distorted octahedron
22
23 within a d⁹-configuration. The Cu^{II}-Cl and Cu^{II}-N bond lengths in **2** are not unusual.
24
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30 The pattern among the bond angles at the metal ions is less straightforward: The N-M-N
31
32 angles of the Cu/S(mmb) (169.8(1)° for **4**) and Ag/Se(psbi) combinations (174.9(2)° for **1**) are
33
34 rather closer to linearity, especially when compared to the 144.4(1)° for the Ag/S(mmb)
35
36 alternative **5**.
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39 As with the M-E distances there is also a wide variety when it comes to E-M-E angles: The
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41 copper(I)/thioether species **4** has an E-M-E angle of 109.33(3)°, the Ag/S combination **5** has
42
43 124.15(4)°, and the new Ag/Se compound **1** exhibits a rather obtuse Se-Ag-Se angle of
44
45 151.94(3)° in agreement with the flattening. Symmetry dictates the Se---Cu^{II}---Se angle in **2** to
46
47 be 180° just as N-Cu-N, the smaller N-Cu-Se angle is 73.53°.
48
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50
51 The chelate bite angles N-M-E show relatively little variation, correlating with the sums of
52
53 the bond distances, (M-N) + (M-E). Accordingly, the silver(I) and copper(II) species exhibit
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55 smaller such angles (< 80°) when compared to the Cu^I compound **4** with 82.47(6)°.
56
57

58
59 The sum of the six angles at the four-coordinate metal ions in compounds **1**, **4**, and **5**
60
reflects the amount of flattening, the values for ideal coordination geometries are 720°
(square-planar), 657° (tetrahedral) and 630° (trigonal-pyramidal). The sums of angles, Σ , as

1
2
3 given in the following, show the exceptional situation for the $[\text{Ag}(\text{psbi})_2]^+$ ion in **1**: $\Sigma = 684.4^\circ$
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5
6 (**1**), 651.2° (**4**), 664.3° (**5**).
7

8 The complex cation in **1** has both the N-Ag-N and Se-Ag-Se angles at rather high values
9
10 ($174.9(2)^\circ$ and $151.94(3)^\circ$, respectively) which produces a significantly flattened situation.
11
12 The Ag/N1/N3/Se1/Se2 best plane shows deviations of $+0.328$ (Ag), $+0.222$ (N1), $+0.236$
13
14 (N3), -0.400 (Se1) and -0.386 \AA (Se2).
15
16

17 To confirm this rather rare flattened form of 2+2 four-coordination [13a], we tried to
18
19 reproduce the substantial features of the experimental structure of $[\text{Ag}(\text{psbi})_2]^+$ by DFT
20
21 calculations (Table 2). DFT slightly overestimates the Se-C distances and underestimates the
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23 Ag-N bond lengths, however, the calculation essentially confirms the unusual geometry of the
24
25 Ag-N bond lengths, however, the calculation essentially confirms the unusual geometry of the
26
27 cation in **1**. This result also suggests that neither intermolecular or packing effects, hydrogen
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29 bonding, ionic forces, or Se---Se interactions are responsible for the curious structural result.
30
31

32 The copper(II) compound **2** makes use of the weakly binding selenoether donor atoms as
33
34 built-in (intramolecular) axial ligands in an otherwise conventional planar Jahn-Teller
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36 situation. Absence of charge, low σ basicity, and poor π back donation to the metal disfavor
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38 the organoselenium substituent as a ligand for copper(II).
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43 *Electrochemistry*

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48 The reversible transition $[\text{Cu}(\text{mmb})_2]^{+/2+}$ as observed by cyclic voltammetry [6] suggested to
49
50 view this complex as a minimal model for type 1 copper centers in blue copper proteins
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52 [12b,17b]. The intricate electron transfer kinetics of copper(I/II) with N and S donor
53
54 containing ligands was studied in detail by Rorabacher et al. [12a]. The selenium compounds
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56 described here showed a variable cyclovoltammetric response, probably due to adsorption
57
58 effects; optimization using a non-coordinating solvent and variations of the internal
59
60 reference/mediator gave satisfactory results.

1
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3 Oxidation of the copper(I) compound **3** in the presence of $\text{Fe}(\text{C}_5\text{H}_5)_2$ or $\text{Fe}(\text{C}_5\text{Me}_5)_2$ as
4 internal standards gave a fully reversible response (Figure 4) at $E_{1/2} = +0.40$ V vs
5 $[\text{Fe}(\text{C}_5\text{H}_5)_2]^{+/0}$ in $\text{CH}_2\text{Cl}_2/0.1$ M Bu_4NBF_4 with $i_a/i_c = 1.0$ and ΔE values increasing from 90
6 mV at 10 mV/s scan rate to 200 mV at 500 mV/s. The potential is thus slightly more positive
7 when compared to the result at +0.31 V under comparable circumstances for the related
8 sulfur-containing compound **4** [6], indicating a somewhat more stable copper(I) state in **3** due
9 the presence of the “softer” selenium. It has been discussed by Samuelson et al. that the
10 optimum balance of copper(I) for harder (e.g. N) and softer donors (e.g. P) is not easily
11 predictable [23].
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27 Figure 4
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32 Although the silver(I) compound **1** with its approximately planar coordination arrangement
33 at the d^{10} -configured metal looked like a suitable candidate for reversible oxidation to the
34 $4d^9$ system silver(II) [24], even low-temperature cyclic voltammetry at 213 K in
35 dichloromethane or *n*-butyronitrile/0.1 M Bu_4NPF_6 did not show any sign of reversible
36 electron loss but only an irreversible oxidation wave at about 1.0 V vs $\text{Fc}^{+/0}$, possibly because
37 of the labile Ag-Se bonds. Expectedly, the dichlorocopper(II) compound **2** was not reduced
38 reversibly due to chloride dissociation.
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48 Concluding, the structural data presented here with M-Se distances longer than 2.9 Å
49 confirm that the phenylselenoether function shows only weak binding to Ag^{I} and Cu^{II} in
50 relation to comparable thioether species. For the copper(II) compound **2** the result is a very
51 pronounced Jahn-Teller situation, i.e. elongation of the coordination octahedron along the Se-
52 Cu-Se axis, whereas the silver(I) system **1** shows a highly distorted four-coordination with a
53 tendency towards flattening. Compound **1** is mononuclear unlike the dinuclear Ag--Ag
54 bonded species $[\text{Ag}_2(\text{msb})_2(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$ formed with the dialkylselenoether ligand $\text{msb} =$
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3 2-methylselenomethyl-*IH*-benzimidazole [10], and it does not show any sign of reversible
4
5 oxidation despite the partially planar arrangement of the AgNNSe atoms. In contrast, the
6
7 oxidation of the analogous [Cu(psbi)₂](BF₄) (**3**) is still reversible just as similar thioether
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9 analogues [6], but only a future structure determination of this or related copper(I) complexes
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11 will indicate whether there is a structural basis for this difference and whether the π acceptor
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13 effect of selenium is operating.
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22 **Experimental Section**

23 *Instrumentation*

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33 ¹H-NMR spectra were taken on a Bruker AC 250 and 400 spectrometers. UV/Vis absorption
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35 spectra were obtained using a J&M Tidas spectrophotometer. Cyclic voltammetry was carried
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37 out in 0.1 M Bu₄NPF₆ solutions using a three-electrode configuration (glassy carbon working
38
39 electrode, Pt counter electrode, Ag/AgCl reference) and a PAR 273 potentiostat and function
40
41 generator. The ferrocene/ferrocenium or decamethylferrocene/decamethylferrocenium couple
42
43 served as internal reference.
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49 *Crystal Structure Determination*

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54 Single crystals were obtained by slow evaporation of an acetonitrile solution in the dark (**1**)
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56 and by overlying a methanol solution with diethyl ether and slow diffusion at 255 K (**2**). The
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58 X-ray data were collected at 188(2) K on a Siemens P4 diffractometer, using graphite
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60 monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) and employing Wyckoff scans. Further

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3 details are given in Table 1. All structures were solved by the Patterson method using the
4
5 SHELXTL package while refinement was carried out with SHELXL97 employing full-matrix
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7 least-squares methods on F^2 with $F\sigma^2 > -2\sigma(F\sigma^2)$ [25]. All non-hydrogen atoms were refined
8
9 anisotropically, hydrogen atoms were introduced using appropriate riding models. CCDC-
10
11 718866 and CCDC-718867 contain the supplementary crystallographic data for this paper.
12
13 These data can be obtained free of charge from The Cambridge Crystallographic Data Centre
14
15 via www.ccdc.cam.ac.uk/data_request/cif.
16
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21

22 **Phenylselenomethyl-1*H*-benzimidazole (psbi)**

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24 An amount of 1.7 g (5.5 mmol) diphenyldiselenide was dissolved in dry ethanol under argon
25
26 and was reduced by adding 0.50 g (13 mmol) of sodium borohydride. After one hour the
27
28 solution had turned colorless and the hydrogen gas evolution had ceased. Then a suspension
29
30 of 1.82 g (11.0 mmol) 2-chloromethyl-1*H*-benzimidazole in ethanol was added and the
31
32 reaction mixture stirred for 10 h. After removal of the solvent the product was isolated by
33
34 column chromatography (silica, ethyl acetate/petrol ether 1:2). 3.2 g (7.4 mmol, 57 %) of the
35
36 colorless psbi were isolated. Anal. Calc. for $C_{14}H_{12}N_2Se$ ($M_W = 287.22$ g/mol) C, 58.54; H,
37
38 4.21; N, 9.75; found C, 58.29; H, 4.46; N, 9.57%. 1H -NMR (CD_3CN): 4.30 s ($J_{Se-H} = 6.9$ Hz);
39
40 7.18-7.10 m; 7.30-7.18 m; 7.60-7.40 m. ^{13}C -NMR (CD_3CN): 24 ($J_{Se-C} = 30$ Hz); 115.7; 122.9;
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42 128.3; 130.1; 133.7; 143.3; 153.1; 153.8. ^{77}Se -NMR (CD_3CN): 351.7.
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50 **[Ag(psbi)₂](BF₄) (1)**

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52 AgBF₄ (17.0 mg, 0.087 mmol) and psbi (50.0 mg, 0.174 mmol) were dissolved in 5 ml
53
54 acetonitrile. Colorless crystals were obtained by storing the solution in a dark place until the
55
56 solvent had evaporated. 53 mg (79%) were isolated. Anal. Calc. for $C_{28}H_{24}AgBF_4N_4Se_2 \cdot H_2O$
57
58 ($M_W = 787.12$ g/mol) C, 42.73; H, 3.33; N, 7.12; found C, 42.20; H, 3.65; N, 7.42%. 1H -NMR
59
60 (CD_3CN): 4.43 s ($J_{Se-H} = 6.9$ Hz); 7.32-7.28 m; 7.36-7.32 m; 7.6-7.5 m; 7.85 s. ^{13}C -NMR

(CD₃CN): 25.9 ($J_{\text{Se-C}} = 30$ Hz); 118.6; 124.4; 127.7; 129.1; 129.5; 130.1; 130.3; 132.5; 133.9; 153.4; 182.7. ⁷⁷Se-NMR (CD₃CN): 330.1.

[CuCl₂(psbi)₂] (2)

CuCl₂ (11.5 mg, 0.087 mmol) was dissolved in 3 ml methanol and mixed with psbi (50.0 mg, 0.174 mmol), also dissolved in 3 ml CH₃OH. Green crystals (42 mg, 70%) were obtained by overlaying the solution with 15 ml of diethylether at -18°C. Anal. Calc. for C₂₈H₂₄Cl₂CuN₄Se₂ ($M_{\text{W}} = 708.89$ g/mol) C, 47.44; H, 3.41; N, 7.90; found C, 46.33; H, 3.41; N 7.75%. UV-VIS (CH₃CN): $\lambda_{\text{max}} = 760$ nm. EPR (MeOH, 110 K): $g_{\parallel} = 2.31$, $g_{\perp} = 2.065$, $A_{\parallel} = 14.8$ mT.

[Cu(psbi)₂](BF₄) (3)

[Cu(CH₃CN)₄](BF₄) (27.3 mg, 0.087 mmol) and psbi (50.0 mg, 0.174 mmol) were dissolved under argon in 5 ml acetonitrile. A volume of 15 ml hexane was added to precipitate 51 mg (0.07 mmol, 80%) of colorless [Cu(psbi)₂](BF₄). Anal. Calc. for C₂₈H₂₄BCuF₄N₄Se₂ · 0.5 H₂O ($M_{\text{W}} = 733.97$ g/mol) C, 45.83; H, 3.44; N, 7.64; found C, 45.71; H 3.75; N 8.01. ¹H-NMR (CD₃CN): 4.36 s ($J_{\text{Se-H}} = 6.9$ Hz); 7.28-7.17 m; 7.35-7.28 m; 7.47-7.39 m; 7.60-7.53 m. ¹³C-NMR (CD₃CN): 26.0 ($J_{\text{Se-C}} = 30$); 117.8; 124.4; 129.0; 129.6; 130.0; 133.5; 163.5; 186.0.

DFT Calculation of [Ag(psbi)₂]⁺

The ground state electronic structure calculation has been done by the density-functional theory (DFT) method using the ADF2007.01 program package [26-28]. Slater type orbital (STO) basis sets of triple- ζ quality with two polarization functions for C, N, Se and Ag and double- ζ quality with one polarization function for H were employed. The inner shells were represented by the frozen core approximation (1s for C, N, 1s-3p for Se and 1s-3d for Ag were kept frozen). The calculations were done with the functional including Becke's gradient

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2
3 correction [29] to the local exchange expression in conjunction with Perdew's gradient
4
5 correction [30] to the local correlation (ADF/BP). The scalar relativistic (SR) zero order
6
7 regular approximation (ZORA) was used within this study. Geometry optimization was done
8
9 without any symmetry constraints.
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Table 1. Crystal and refinement data for complexes psbi-Ag und psbi-Cu

empirical formula	$C_{28}H_{24}AgBF_4N_4Se_2$	$C_{28}H_{24}Cl_2CuN_4Se_2$
molar mass	769.11	708.88
temperature (K)	173(2)	173(2)
wavelength (Å)	0.71073	0.71073
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
cell dimensions (Å)	$a = 10.010(2)$	$a = 9.572(2)$
	$b = 10.067(2)$	$b = 12.661(2)$
	$c = 15.628(3)$	$c = 11.667(3)$
	$\alpha = 102.23(3)^\circ$	$\beta = 102.29(2)^\circ$
	$\beta = 108.06(3)^\circ$	
	$\gamma = 100.24(3)^\circ$	
cell volume (Å ³)	1412.2(5)	1381.5(5)
Z	2	2
calc. density (Mg/m ³)	1.809	1.704
absorption coefficient (mm ⁻¹)	3.344	3.644
F(000)	752	702
measured Θ region (°)	2.14-52.00	2.18-55.00
index region	$-11 \leq h \leq 12, -12 \leq k \leq 12$	$0 \leq h \leq 12, 0 \leq k \leq 16$
	$-19 \leq l \leq 18$	$-15 \leq l \leq 14$
no of reflections	5586	3355
no of independent reflections	4023 [$R_{int} = 0.0757$]	3171 [$R_{int} = 0.0463$]
absorption correction	empirical	empirical

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3	data/restraints/parameters	4023 / 0 / 369	3171 / 0 / 180
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5	goodness-of-fit on F^2	1.174	1.329
6			
7	final R values [$I > 2\sigma(I)$]	R1 = 0.0505,	R1 = 0.0456,
8		wR2 = 0.1184	wR2 = 0.0991
9			
10	R values (all data)	R1 = 0.0757, wR2 = 0.1315	R1 = 0.0712, wR2 = 0.1106
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12	max/min electron density ($e\text{\AA}^{-3}$)	1.054; -0.986	1.044; -0.599
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Table 2. Comparison of Selected Calculated and Experimental Bond Parameters in the Crystal of [Ag(psbi)₂](BF₄) (**1**)

Bond lengths	Experimental	Calculated
Ag-N1	2.249(4)	2.215
Ag-N3	2.252(4)	2.218
Ag-Se1	2.923(1)	2.952
Ag-Se2	3.040(1)	3.021
Se1-C9	1.955(6)	1.985
Se1-C10	1.937(6)	1.946
Se2-C29	1.968(5)	1.975
Se2-C30	1.917(8)	1.941
Bond angles	Experimental	Calculated
N1-Ag-N3	174.9(2)	175.4
N1-Ag-Se1	76.6(1)	79.1
N3-Ag-Se1	102.0(1)	102.9
N1-Ag-Se2	103.6(1)	102.8
N3-Ag-Se2	75.3(1)	77.7
Se1-Ag-Se2	151.94(3)	149.6
C9-Se1-Ag	92.0(2)	88.5
C10-Se1-Ag	104.1(2)	106.2
C29-Se2-Ag	89.6(2)	87.4
C30-Se2-Ag	90.6(2)	95.5
C9-Se1-C10	99.0(2)	100.9
C29-Se2-C30	101.3(3)	102.4

Table 3. Selected Bond Parameters of [Cu(psbi)₂Cl₂] (**2**)

2	
Bond lengths	
Cu-N3	1.997(3)
Cu-Cl	2.299(1)
Cu-Se	3.2944(8)
Se-C10	1.956(4)
Se-C11	1.914(5)
C2-C10	1.476(5)
N3-C2	1.352(5)
Bond angles	
N3-Cu-N3'	180.0
Se-Cu-Se'	180.0
N3-Cu-Se/Se'	73.53(8)/106.47(8)
C2-N3-Cu	125.9(3)
C10-Se-C11	100.3(2)
N3-Cu-Cl/Cl'	89.55(9)/90.45(9)
Cl-Cu-Cl	180.0

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3 **Figure captions**
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5

6 **Figure 1.** Molecular structure of the complex cation in the crystal of $[\text{Ag}(\text{psbi})_2](\text{BF}_4)$ (**1**).
7

8 **Figure 2.** Molecular structure of $[\text{Cu}(\text{psbi})_2\text{Cl}_2]$ (**2**) in the crystal.
9

10 **Figure 3.** Arrangement of molecules **2** in the crystal.
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12 **Figure 4.** Cyclic voltammogram of compound $[\text{Cu}(\text{psbi})_2](\text{BF}_4)$ in dichloromethane/0.1 M
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14 Bu_4NBF_4 at 50 mV/s scan rate (*: decamethylferrocene as internal standard).
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Figure 1

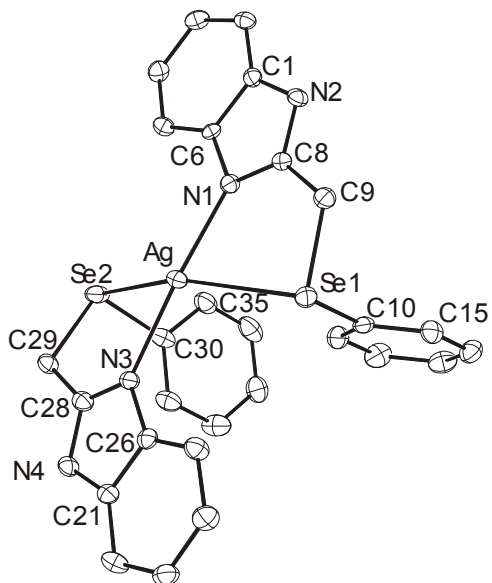


Figure 2

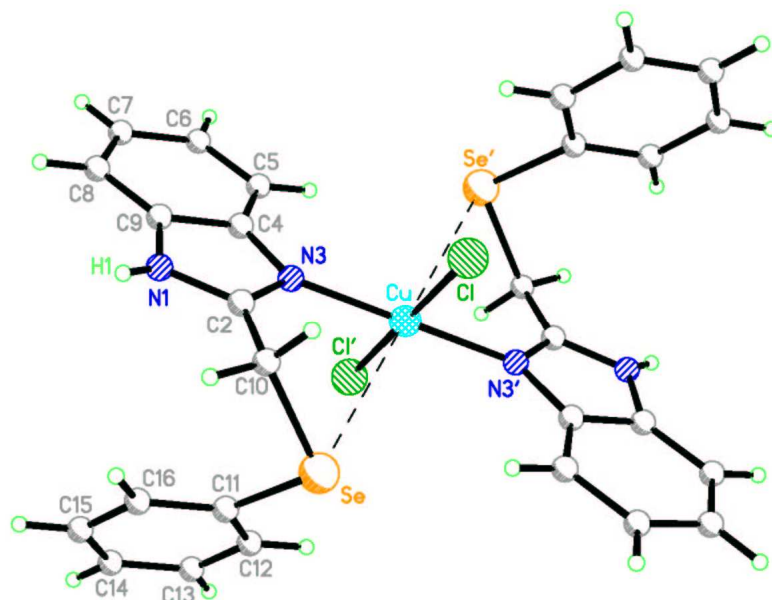
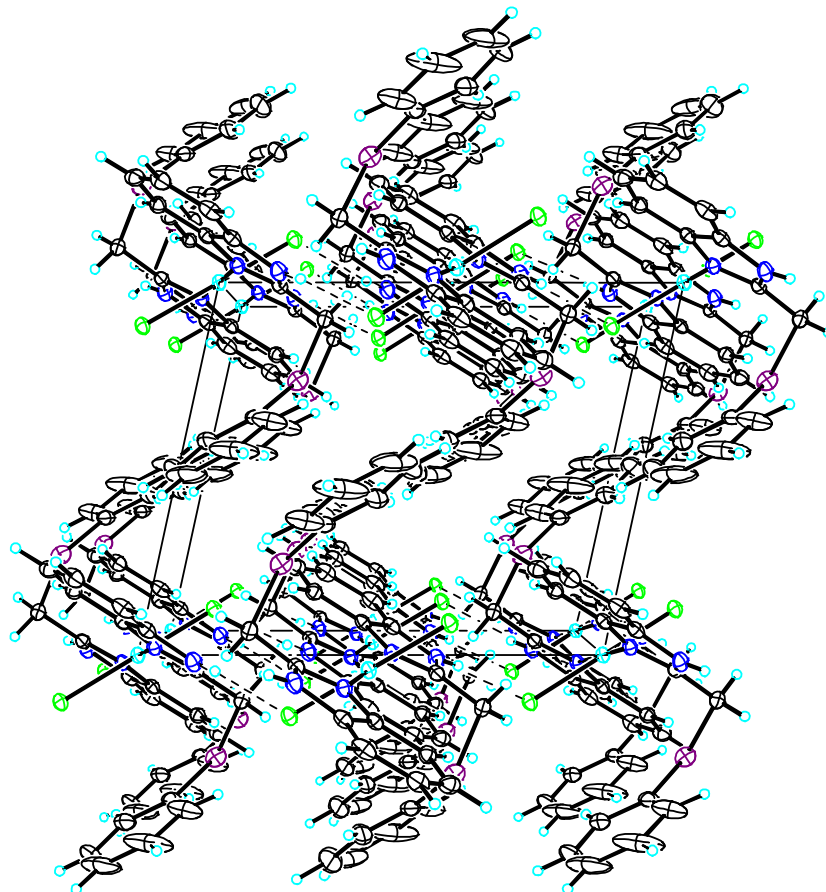


Figure 3



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Figure 4

