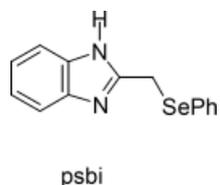
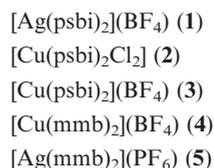


In addition to the biochemical context related to the function of thioethers [17], molecular copper complexes of sulfur- or selenium-containing ligands [2] may be of interest as potential precursor components for obtaining copper/indium/gallium selenide or sulfide (CIGS) photovoltaic materials CuME_2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

We now report a selenium-containing ligand related to *mmb*, viz., 2-phenylselenomethyl-1*H*-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).



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.

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

The bidentate *psbi* ligand, offering a benzimidazole imino function and an aryl alkyl selenoether donor, was obtained in a straightforward way. The arylseleno function is helpful for obtaining mononuclear complexes, the analogous *dialkyl* selenoether ligand 2-methylselenomethyl-1*H*-benzimidazole gave a disilver(I) species with an $\text{Ag}\cdots\text{Ag}$ distance of 3.156(1) Å [10].

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

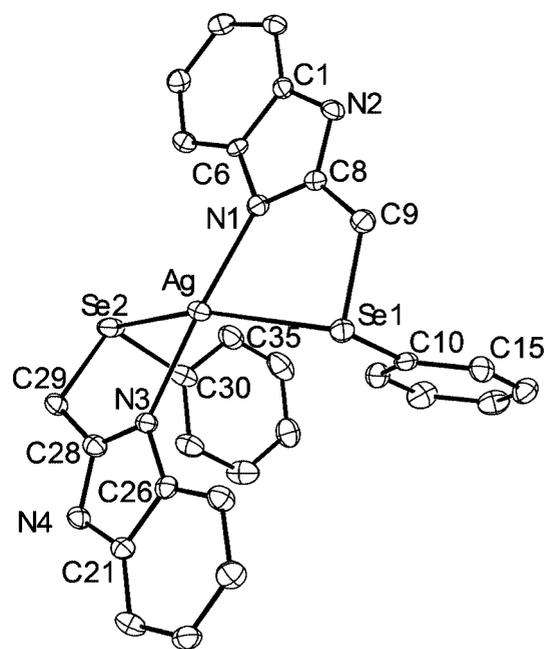


Figure 1. Molecular structure of the complex cation in the crystal of $[\text{Ag}(\text{psbi})_2](\text{BF}_4)$ (**1**).

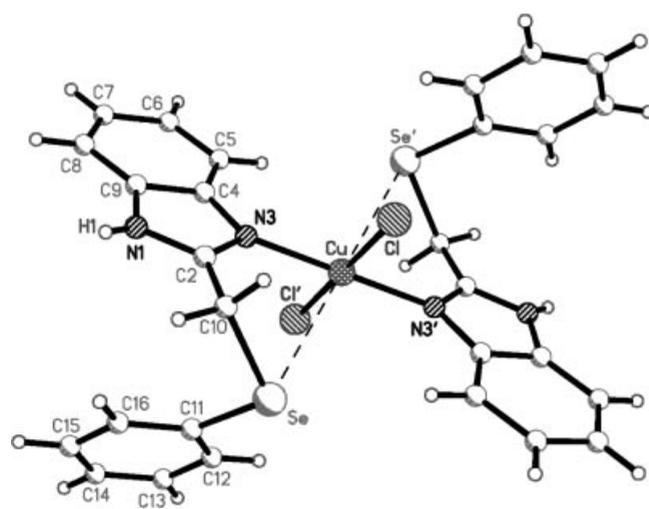


Figure 2. Molecular structure of $[\text{Cu}(\text{psbi})_2\text{Cl}_2]$ (**2**) in the crystal.

The two new structures do not show unusual intermolecular interactions. Hydrogen bonding $\text{NH}\cdots\text{F}$ from the benzimidazole-NH to the counterions [1: 2.837(8) Å for $\text{N4}(\text{H})\cdots\text{F3}(\text{BF}_4)$ as shortest such distance] and rather marginal [19, 21] intermolecular $\text{Se}\cdots\text{Se}$ 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 $\text{N}(\text{H})\cdots\text{Cl}(\text{Cu})$ 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 CH_2SePh substituents either above and below (**2**) or both above (**1**) that plane.

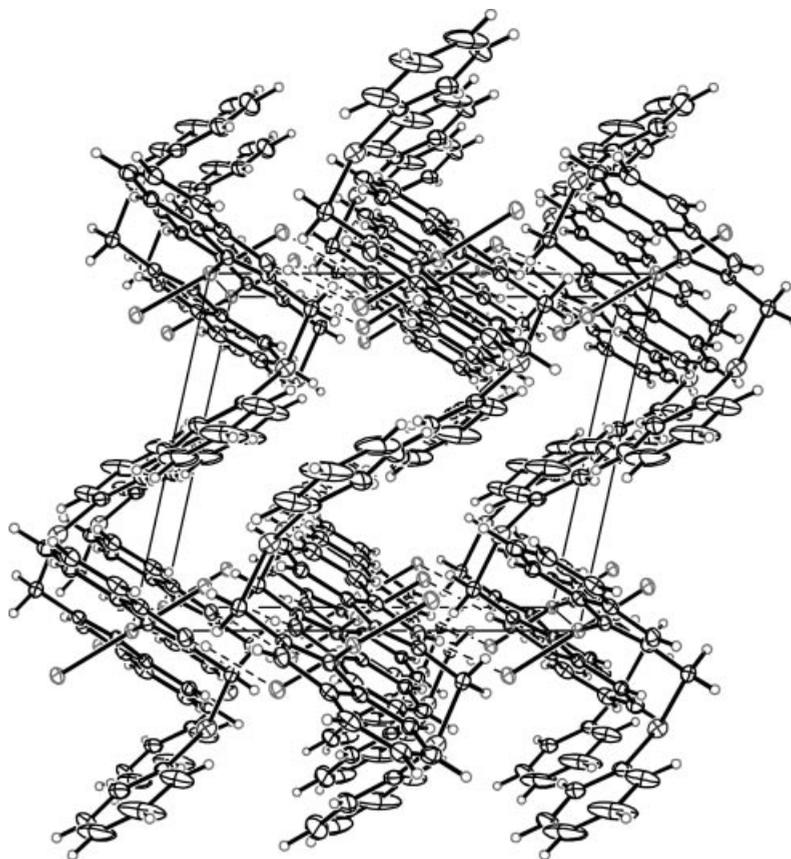


Figure 3. Arrangement of molecules 2 in the crystal.

Table 1. Crystal and refinement data for complexes 1 and 2.

Empirical formula	C ₂₈ H ₂₄ AgBF ₄ N ₄ Se ₂	C ₂₈ H ₂₄ Cl ₂ CuN ₄ Se 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	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
Cell dimensions /Å	<i>a</i> = 10.010(2) <i>b</i> = 10.067(2) <i>c</i> = 15.628(3) α = 102.23(3)° β = 108.06(3)° γ = 100.24(3)°	<i>a</i> = 9.572(2) <i>b</i> = 12.661(2) <i>c</i> = 11.667(3) β = 102.29(2)°
Cell volume /Å ³	1412.2(5)	1381.5(5)
<i>Z</i>	2	2
Calcd. density /Mg·m ⁻³	1.809	1.704
Absorption coefficient /mm ⁻¹	3.344	3.644
<i>F</i> (000)	752	702
Measured θ region /°	2.14–52.00	2.18–55.00
Index region	–11 ≤ <i>h</i> ≤ 12 –12 ≤ <i>k</i> ≤ 12 –19 ≤ <i>l</i> ≤ 18	0 ≤ <i>h</i> ≤ 12 0 ≤ <i>k</i> ≤ 16 –15 ≤ <i>l</i> ≤ 14
No. of reflections	5586	3355
No. of independent reflections	4023 [<i>R</i> _{int} = 0.0757]	3171 [<i>R</i> _{int} = 0.0463]
Absorption correction	empirical	empirical
Data/restraints/parameters	4023/0/369	3171/0/180
Goodness-of-fit on <i>F</i> ²	1.174	1.329
Final <i>R</i> values [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0505, <i>wR</i> ₂ = 0.1184	<i>R</i> ₁ = 0.0456, <i>wR</i> ₂ = 0.0991
<i>R</i> values (all data)	<i>R</i> ₁ = 0.0757, <i>wR</i> ₂ = 0.1315	<i>R</i> ₁ = 0.0712, <i>wR</i> ₂ = 0.1106
max/min electron density /e·Å ⁻³	1.054; –0.986	1.044; –0.599

Table 2. Comparison of selected calculated and experimental bond parameters in Å and ° 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 in Å and ° 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

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**) to Ag⁺ (**1,5**), reflecting the difference (1.26 Å–0.96 Å) of the ionic radii [22]. On the other hand, the copper(II)–N(imine) bond in **2** is typically longer than the copper(I)–N(imine) bond in **4** because of absent π back donation. The M–E distances (E = S or Se) show substantial increase between the complexes of Cu⁺ (**4**) or Ag⁺ (**1,5**) and mmb (**4,5**) or psbi ligands (**1**). Remarkably, the cations

in the crystal of [Ag(psbi)₂](BF₄) exhibit two quite different Ag–Se distances at 2.923(1) and 3.040(1) Å, indicating structural flexibility of this weak bonding (shallow energy surface); the sum of the van der Waals radii of Se and Ag is about 3.60 Å [22]. The difference to the Ag–S distance of 2.7019(8) Å in **5** [8] is striking. The still longer Cu^{II}···Se distance in **2** corresponding to the sum of the van der Waals radii at 3.30 Å [22] illustrates the familiar tetragonal stretching of a Jahn–Teller distorted octahedron within a d⁹-configuration. The Cu^{II}–Cl and Cu^{II}–N bond lengths in **2** are not unusual.

The pattern among the bond angles at the metal ions is less straightforward: The N–M–N angles of the Cu/S(mmb) [169.8(1)° for **4**] and Ag/Se(psbi) combinations [174.9(2)° for **1**] are rather closer to linearity, especially when compared to the 144.4(1)° for the Ag/S(mmb) alternative **5**.

As with the M–E distances there is also a wide variety when it comes to E–M–E angles: The copper(I)/thioether species **4** has an E–M–E angle of 109.33(3)°, the Ag/S combination **5** has 124.15(4)°, and the new Ag/Se compound **1** exhibits a rather obtuse Se–Ag–Se angle of 151.94(3)° in agreement with the flattening. Symmetry dictates the Se···Cu^{II}···Se angle in **2** to be 180° just as N–Cu–N, the smaller N–Cu–Se angle is 73.53°.

The chelate bite angles N–M–E show relatively little variation, correlating with the sums of the bond lengths, (M–N) + (M–E). Accordingly, the silver(I) and copper(II) species exhibit smaller such angles (< 80°) when compared to the Cu^I compound **4** with 82.47(6)°.

The sum of the six angles at the four-coordinate metal ions in compounds **1**, **4**, and **5** 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 given in the following, show the exceptional situation for the [Ag(psbi)₂]⁺ ion in **1**: Σ = 684.4° (**1**), 651.2° (**4**), 664.3° (**5**).

The complex cation in **1** has both the N–Ag–N and Se–Ag–Se angles at rather high values [174.9(2)° and 151.94(3)°, respectively] which produces a significantly flattened situation. The Ag/N1/N3/Se1/Se2 best plane shows deviations of +0.328 (Ag), +0.222 (N1), +0.236 (N3), –0.400 (Se1) and –0.386 Å (Se2).

To confirm this rather rare flattened form of 2+2 four-coordination [13a], we tried to reproduce the substantial features of the experimental structure of [Ag(psbi)₂]⁺ by DFT calculations (Table 2). DFT slightly overestimates the Se–C distances and underestimates the Ag–N bond lengths, however, the calculation essentially confirms the unusual geometry of the cation in **1**. This result also suggests that neither intermolecular or packing effects, nor hydrogen bonding, ionic forces or Se···Se interactions are responsible for the curious structural result.

The copper(II) compound **2** makes use of the weakly binding selenoether donor atoms as built-in (intramolecular) axial ligands in an otherwise conventional planar Jahn–Teller situation. Absence of charge, low σ basicity,

and poor π back donation to the metal disfavor the organo-selenium substituent as a ligand for copper(II).

Electrochemistry

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

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 internal standards gave a fully reversible response (Figure 4) at $E_{1/2} = +0.40$ V vs. $[\text{Fe}(\text{C}_5\text{H}_5)_2]^{+/0}$ in $\text{CH}_2\text{Cl}_2/0.1$ M Bu_4NPF_6 with $i_a/i_c = 1.0$ and ΔE values increasing from 90 mV at 10 mV/s scan rate to 200 mV at 500 mV/s. The potential is thus slightly more positive when compared to the result at +0.31 V under comparable circumstances for the related sulfur-containing compound **4** [6], indicating a somewhat more stable copper(I) state in **3** due the presence of the “softer” selenium. It has been discussed by *Samuelson et al.* that the optimum balance of copper(I) for harder (e.g.; N) and softer donors (e.g.; P) is not easily predictable [23].

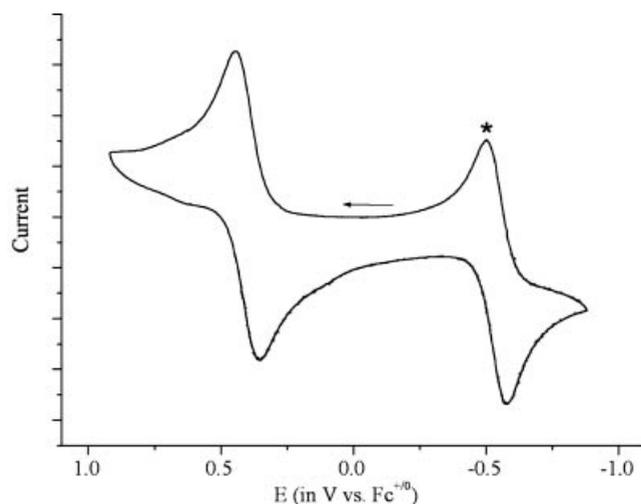


Figure 4. Cyclic voltammogram of compound $[\text{Cu}(\text{psbi})_2](\text{BF}_4)$ in dichloromethane/0.1 M Bu_4NPF_6 at 50 $\text{mV}\cdot\text{s}^{-1}$ scan rate (*: decamethylferrocene as internal standard).

Although the silver(I) compound **1** with its approximately planar coordination arrangement at the d^{10} -configured metal looked like a suitable candidate for reversible oxidation to the $4d^9$ system silver(II) [24], even low-temperature cyclic voltammetry at 213 K in dichloromethane or *n*-butyronitrile/0.1 M Bu_4NPF_6 did not show any sign of reversible electron loss but only an irreversible oxidation wave at about 1.0 V vs. $\text{Fc}^{+/0}$, possibly because of the labile

Ag–Se bonds. Expectedly, the dichloridocopper(II) compound **2** was not reduced reversibly due to chloride dissociation.

Concluding, the structural data presented here with M–Se distances longer than 2.9 Å confirm that the phenyl selenoether function shows only weak binding to Ag^I and Cu^{II} in relation to comparable thioether species. For the copper(II) compound **2** the result is a very pronounced Jahn–Teller situation, i.e. elongation of the coordination octahedron along the Se–Cu–Se axis, whereas the silver(I) system **1** shows a highly distorted four-coordination with a tendency towards flattening. Compound **1** is mononuclear unlike the dinuclear Ag \cdots Ag bonded species $[\text{Ag}_2(\text{msb})_2(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$ formed with the dialkyl selenoether ligand msb = 2-methylselenomethyl-1*H*-benzimidazole [10], and it does not show any sign of reversible oxidation despite the partially planar arrangement of the AgNNSe atoms. In contrast, the oxidation of the analogous $[\text{Cu}(\text{psbi})_2](\text{BF}_4)$ (**3**) is still reversible just as similar thioether analogues [6], but only a future structure determination of this or related copper(I) complexes will indicate whether there is a structural basis for this difference and whether the π acceptor effect of selenium is operating.

Experimental Section

Instrumentation: ¹H NMR spectra were taken with Bruker AC 250 and 400 spectrometers. UV/Vis absorption spectra were obtained using a J&M Tidas spectrophotometer. Cyclic voltammetry was carried out in 0.1 M Bu_4NPF_6 solutions using a three-electrode configuration (glassy carbon working electrode, platinum counter electrode, Ag/AgCl reference) and a PAR 273 potentiostat and function generator. The ferrocene/ferrocenium or decamethylferrocene/decamethylferrocenium couple served as internal reference.

Crystal Structure Determination: Single crystals were obtained by slow evaporation of an acetonitrile solution in the dark (**1**) and by overlying a methanol solution with diethyl ether and slow diffusion at 255 K (**2**). The X-ray data were collected at 188(2) K with a Siemens P4 diffractometer, using graphite-monochromated Mo- K_α radiation ($\lambda = 0.71073$ Å) and employing Wyckoff scans. Further details are given in Table 1. All structures were solved by the Patterson method using the SHELXTL package while refinement was carried out with SHELXL97 employing full-matrix least-squares methods on F^2 with $F\sigma^2 > -2\sigma(F\sigma^2)$ [25]. All non-hydrogen atoms were refined anisotropically, hydrogen atoms were introduced using appropriate riding models. CCDC-718866 and CCDC-718867 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Phenylselenomethyl-1*H*-Benzimidazole (psbi): Diphenyl diselenide (1.7 g, 5.5 mmol) was dissolved in dry ethanol under argon and was reduced by adding sodium borohydride (0.50 g, 13 mmol). After one hour the solution had turned colorless and the hydrogen gas evolution had ceased. Then a suspension of 2-chloromethyl-1*H*-benzimidazole (1.82 g, 11.0 mmol) in ethanol was added and the reaction mixture stirred for 10 h. After removal of the solvent the product was isolated by column chromatography (silica, ethyl acetate/petroleum ether, 1:2). 3.2 g (7.4 mmol, 57 %) of the color-

less psbi were isolated. $C_{14}H_{12}N_2Se$ (287.22): calcd. C 58.54, H 4.21, N 9.75; found C 58.29, H 4.46, N 9.57. 1H NMR (CD_3CN): $\delta = 4.30$ (s, $J_{Se-H} = 6.9$ Hz), 7.18–7.10 (m), 7.30–7.18 (m), 7.60–7.40 (m). ^{13}C NMR (CD_3CN): $\delta = 24$ ($J_{Se-C} = 30$ Hz), 115.7, 122.9, 128.3, 130.1, 133.7, 143.3, 153.1, 153.8. ^{77}Se NMR (CD_3CN): $\delta = 351.7$.

[Ag(psbi) $_2$](BF $_4$) (1): AgBF $_4$ (17.0 mg, 0.087 mmol) and psbi (50.0 mg, 0.174 mmol) were dissolved in acetonitrile (5 mL). Colorless crystals were obtained by storing the solution in a dark place until the solvent had evaporated. 53 mg (79%) were isolated. $C_{28}H_{24}AgBF_4N_4Se_2 \cdot H_2O$ (787.12): calcd. C 42.73, H 3.33, N 7.12; found C 42.20, H 3.65, N 7.42. 1H NMR (CD_3CN): $\delta = 4.43$ (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 (CD_3CN): $\delta = 25.9$ ($J_{Se-C} = 30$ Hz), 118.6, 124.4, 127.7, 129.1, 129.5, 130.1, 130.3, 132.5, 133.9, 153.4, 182.7. ^{77}Se NMR (CD_3CN): $\delta = 330.1$.

[CuCl $_2$ (psbi) $_2$] (2): CuCl $_2$ (11.5 mg, 0.087 mmol) was dissolved in methanol (3 mL) and mixed with psbi (50.0 mg, 0.174 mmol), also dissolved in methanol (3 mL). Green crystals (42 mg, 70%) were obtained by overlaying the solution with of ethyl ether (15 mL) at -18 °C. $C_{28}H_{24}Cl_2CuN_4Se_2$ (708.89): calcd. C 47.44, H 3.41, N 7.90; found C 46.33, H 3.41, N 7.75. UV/Vis (CH_3CN): $\lambda_{max} = 760$ nm. EPR (MeOH, 110 K): $g_{||} = 2.31$, $g_{\perp} = 2.065$, $A_{||} = 14.8$ mT.

[Cu(psbi) $_2$](BF $_4$) (3): [Cu(CH_3CN) $_4$](BF $_4$) (27.3 mg, 0.087 mmol) and psbi (50.0 mg, 0.174 mmol) were dissolved under argon in acetonitrile (5 mL). Hexane (15 mL) was added to precipitate 51 mg (0.07 mmol, 80%) of colorless [Cu(psbi) $_2$](BF $_4$). $C_{28}H_{24}BCuF_4N_4Se_2 \cdot 0.5H_2O$ (733.97): calcd. C 45.83, H 3.44, N 7.64; found C 45.71, H 3.75, N 8.01. 1H NMR (CD_3CN): $\delta = 4.36$ s ($J_{Se-H} = 6.9$ Hz), 7.28–7.17 (m), 7.35–7.28 (m), 7.47–7.39 (m), 7.60–7.53 (m). ^{13}C NMR (CD_3CN): $\delta = 26.0$ ($J_{Se-C} = 30$ Hz), 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 correction [29] to the local exchange expression in conjunction with Perdew's gradient correction [30] to the local correlation (ADF/BP). The scalar relativistic (SR) zero order regular approximation (ZORA) was used within this study. Geometry optimization was done without any symmetry constraints.

Acknowledgement

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