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Markus Leboschka, Monika Sieger, Biprajit Sarkar, Jürgen Heck, Mark Niemeyer, et al.. 2-Organoselenomethyl-1H-benzimidazole Complexes of Copper(II) and Copper(I). *Journal of Inorganic and General Chemistry / Zeitschrift für anorganische und allgemeine Chemie*, 2009, 635 (13-14), pp.2177. 10.1002/zaac.200900265 . hal-00515811

HAL Id: hal-00515811

<https://hal.science/hal-00515811>

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Journal:	<i>Zeitschrift für Anorganische und Allgemeine Chemie</i>
Manuscript ID:	zaac.200900265.R1
Wiley - Manuscript type:	Article
Date Submitted by the Author:	03-Jul-2009
Complete List of Authors:	Leboschka, Markus Sieger, Monika Sarkar, Biprajit Heck, Jürgen Niemeyer, Mark Bubrin, Denis Lissner, Falk Schleid, Thomas Zalis, Stanislav Su, Cheng-Yong Kaim, Wolfgang; Institute of Inorganic Chemistry, Stuttgart University
Keywords:	Coordination geometries, Copper compounds, Imidazole ligands, Selenoether ligands



2-Organoselenomethyl-1*H*-benzimidazole Complexes of Copper(II) and Copper(I)

Markus Leboschka,^[a] Monika Sieger,^[a] Biprajit Sarkar,^[a] Jürgen Heck,^[a] Mark Niemeyer,^[b] Denis Bubrin,^[a] Falk Lissner,^[a] Thomas Schleid,^[a] Stanislav Zálíš,^[c] Cheng-Yong Su,^[d] and Wolfgang Kaim^{[a],*}

Stuttgart, Institut für Anorganische Chemie

Received

Dedicated to Professor Martin Jansen on the Occasion of his 65th Birthday

Abstract. Structurally characterized 2-methylselenomethyl-1*H*-benzimidazole (msbi) is shown to form complexes in 2:1 ratio with copper(II). Whereas the central cation $[\text{Cu}(\text{msbi})_2\text{Cl}]^+ = \mathbf{1}^+$ in $[\text{Cu}(\text{msbi})_2\text{Cl}]\text{Cl}\cdot 2 \text{ MeOH}$ crystallizes in an approximately mixed

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3 square-pyramidal/trigonal-bipyramidal structure ($\tau = 0.52$) with the second and third row
4 atoms Cl and Se in the equatorial plane, the related $[\text{Cu}(\text{msbi})_2(\text{MeOH})](\text{BF}_4)_2 = [\mathbf{2}](\text{BF}_4)_2$
5
6 exhibits a closer to square-pyramidal arrangement with $\tau = 0.36$ for that complex dication $\mathbf{2}^{2+}$.
7
8 In both cases, the Cu-N bonds are short at about 1.94 Å while the Cu-Se distances vary
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10 between 2.62 Å for $\mathbf{1}^+$ and ca. 2.54 Å for $\mathbf{2}^{2+}$. Slight differences between the Jahn-Teller
11
12 influenced species $\mathbf{1}^+$ and $\mathbf{2}^{2+}$ are also apparent from absorption and EPR spectra. Since
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14 copper(I) complexes of msbi suitable for crystal structure analysis could not be obtained, the
15
16 related 1-methyl-2-phenylselenomethyl-*IH*-benzimidazole (mpsbi) was prepared and used to
17
18 obtain $[\text{Cu}(\text{mpsbi})_2](\text{x}) = [\mathbf{3}](\text{x})$, $\text{x} = \text{BF}_4$ or PF_6 . The copper(I) ion in the corresponding cation
19
20 $\mathbf{3}^+$ shows a DFT-reproduced distorted tetrahedral configuration with an N-Cu^I-N angle at
21
22 146.7(3)°, less straightened than the ca. 170° in comparable Cu^I complexes with thioether-*IH*-
23
24 benzimidazole ligands. A copper(I) compound $[\text{Cu}(\text{psbi})_2][\text{Cu}(\text{psbi})(\text{psbi-H}^+)](\text{PF}_6) =$
25
26 $[\mathbf{4}^+](\text{PF}_6)$ with another related ligand, 2-phenylselenomethyl-*IH*-benzimidazole (psbi), was
27
28 crystallized in partially benzimidazole-deprotonated acetonitrile solvate form, showing short
29
30 Cu-N bonds of 1.898(5) Å, an N-Cu^I-N angle of 157.5(3)°, a Se--Se interaction at 3.6237(3)
31
32 Å, and a very small Se-Cu-Se angle of 78.23(4)°. The different responses resulting from
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34 thioether and selenoether coordination to copper in the complexes at hand are being
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36 discussed.
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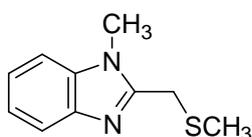
48 **Keywords:** Coordination geometries; Copper compounds; Imidazole ligands; Selenoether
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50 ligands
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54 Introduction

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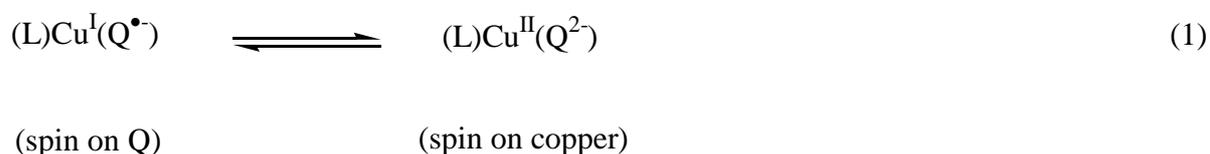
59 Organoselenium ligands are being increasingly used in coordination chemistry [1,2] due to the
60 biological function of this chalcogen [3,4]. Whereas the main focus has been on the important

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3 biological roles of the easily deprotonated selenocysteine, the "21st essential amino acid" [4],
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5 selenomethionine [5] and related selenoethers have been used as probes for NMR
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7 spectroscopic and X-ray crystallographic studies of biomolecules [5]. Following our work on
8
9 copper(I) and copper(II) complexes of mixed imine-N and thioether-S chelate ligands such as
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11 1-methyl-2-(methylthiomethyl)-*1H*-benzimidazole (mmb) [6-8] we have now extended this
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13 approach to related imine-N/selenoether-Se ligands.
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mmb

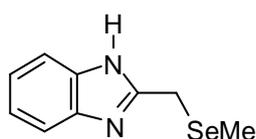
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30 The mmb and related ligands have not only allowed us to observe [9] the biochemically
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32 relevant [10] valence-tautomer equilibrium (Equation 1) outside of an enzyme [6], it also
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34 displayed a remarkable propensity to allow for facile Cu^{II} transitions [6-11] because of
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36 uncommon coordination geometries such as illustrated by a "see-saw" configuration [12]
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38 around the metal in [Cu(mmb)₂]⁺ with its 2+2 coordination arrangement (see Fig. 7 below)
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42 [6].
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54 In addition to the variation in the "minimal modeling" of certain biochemical functions,
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56 molecular copper complexes of sulfur and selenium containing ligands [2] are also of interest
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58 as potential precursor components for obtaining copper/indium/gallium/selenide or -sulfide
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60 (CIGS) photovoltaic materials CuMSe₂ (M = In, Ga) [13].

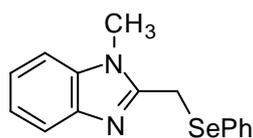
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3 The coordination of thioether and selenoether functions to transition metals has been
4 reviewed and discussed with respect to the π acceptor influence [1b,14], while recent results
5 of methionine-rich copper(I) metalloproteins with regulatory and other functions [15] also
6 stimulate studies in the field. Following the high-resolution protein structure analysis [16] of
7 the monooxygenase enzyme PHM in the presence of bound O₂ there have been several studies
8 reported on mixed imidazole-thioether model ligands and their copper complexes [17].
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17 Using the previously [8a] introduced 2-methylselenomethyl-*1H*-benzimidazole (msbi)
18 ligand we report here results from studies of the copper(I) and copper(II) coordination
19 ligand we report here results from studies of the copper(I) and copper(II) coordination
20 chemistry of that ligand.
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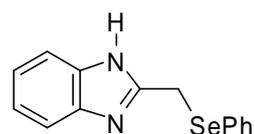


msbi

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37 The inability to obtain a copper(I) complex of msbi suitable for crystal structure analysis
38 prompted us to modify the 2-selenoether-*1H*-benzimidazole chelate system. A structurally
39 characterized copper(I) complex of the new 1-methyl-2-phenylselenomethyl-*1H*-
40 benzimidazole (mpsbi) without the potential for N-H hydrogen bonding was thus obtained
41 and its configuration confirmed by a DFT calculation.
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mpsbi



psbi

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3 Another copper(I) complex ion $[\text{Cu}(\text{psbi})_2]^+$ was obtained from the previously described
4 [8b] ligand 2-phenylselenomethyl-*IH*-benzimidazole = psbi. Whereas the tetrafluoroborate
5 salt could not be crystallized for structure analysis [8b], a single crystalline material was
6 isolated in the presence of hexafluorophosphate. The structure analysis revealed a low anion
7 content attributed to a partial deprotonation of the benzimidazole groups, a behaviour which is
8 not uncommon in the coordination chemistry of imidazole-containing ligands [18,19]. The
9 following copper compounds were studied structurally:
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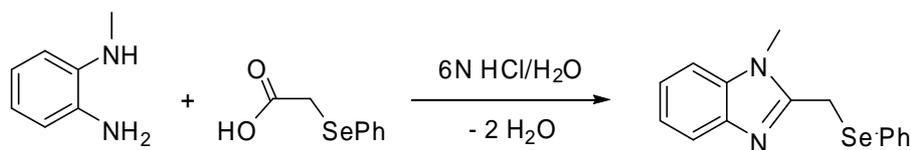
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32 Compounds also described are



33 34 35 36 37 38 39 40 41 42 43 44 45 46 **Results and Discussion**

47 48 49 50 *Ligand synthesis and structure*

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55 The preparations of msbi and psbi via 2-chloromethyl-*IH*-benzimidazole have been reported
56 [8]. The mpsbi ligand was obtained similarly or by reacting *N*-methyl-*o*-phenylenediamine
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58
59
60 with 2-phenylselenoacetic acid (see Exp. Section).



A structure determination of msbi (Table 1, Figure 1) revealed the expected non-planar conformation of the molecule in the crystal with typical bond parameters [20].

Table 1

Figure 1

Copper(II) complexes of msbi

Two different reactions of msbi with copper(II) precursors led to different crystalline materials. The reaction of msbi with CuCl_2 in methanol produced crystallographically characterized $[\text{Cu}(\text{msbi})_2\text{Cl}]\text{Cl}\cdot 2 \text{ MeOH}$ (Figure 2, Tables 1,2) while the reaction with $\text{Cu}(\text{BF}_4)_2$ yielded $[\text{Cu}(\text{msbi})_2(\text{MeOH})](\text{BF}_4)_2$ (Figure 3, Tables 1,2).

Figures 2,3

Table 2

Structurally, both copper(II) complex ions should be affected by ligand-caused effects, i.e. by the chelate bite within the five-membered metallacycle situation and by the considerable asymmetry between the hard, basic imidazole-N and the softer, assumedly [14] π accepting selenoether-Se donor atoms.

The main feature striking in a comparative discussion of the two complexes is a mixed trigonal-bipyramidal/square-pyramidal structure ($\tau = 0.52$ [21]) of the central cation 1^+ with

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3 the second and third row atoms Cl and Se in the equatorial plane, whereas the related
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5 [Cu(msbi)₂(MeOH)](BF₄)₂ exhibits a closer to square-pyramidal arrangement (Figure 4) with
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7
8 $\tau = 0.36$ for the complex dication $\mathbf{2}^{2+}$. The parameter τ is defined as the difference between
9
10 the basal *trans* angles, divided by 60°. A value of $\tau = 0^\circ$ holds for the ideal square-pyramidal
11
12 situation, a value of $\tau = 1$ is calculated for the ideal trigonal-bipyramidal case [21]). Although
13
14 the Se-Cu-Se angle in $\mathbf{1}^+$ is therefore decreased to about 137.75(2)° from 150.6(1)° in $\mathbf{2}^{2+}$, the
15
16 Se--Se distance is beyond any interaction range at >4.5 Å. In both cases the Cu-N bonds are
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18 short at about 1.94 Å while the Cu-Se distances vary between 2.62 Å for $\mathbf{1}^+$ and ca. 2.54 Å for
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23 $\mathbf{2}^{2+}$.

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27 Figure 4

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32 The observed difference in structure for both Cu^{II}(psbi)₂ structures $\mathbf{1}^+$ and $\mathbf{2}^{2+}$ points to a
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34 sensitive situation with two strong Cu^{II}-N(imine) bonds, two weak Cu^{II}-Se(selenoether)
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36 interactions between a hard electrophile and two soft nucleophiles, and an additional donor
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38 with (Cl⁻) or without (MeOH) charge. At 2.167(4) Å the Cu-O distance for bound methanol in
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40 $\mathbf{2}^{2+}$ is relatively short [22], the MeOH...FBF₃ hydrogen bonding at a shortest O...F distance of
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42 2.99 Å lies in a typical range [8a,23,24]. The solvate molecules in [$\mathbf{1}$](Cl)₂·2 MeOH are
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44 connected to the non-coordinated chloride anion (Figure 2) via Cl...HO hydrogen bonds at
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46 Cl...O distance of 3.109(3) Å.

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51 Slight differences between $\mathbf{1}^+$ and $\mathbf{2}^{2+}$ are also apparent from absorption and ESR spectra.
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53 Overall, the spectroscopy of the copper(II) compounds did not yield unusual results. Both
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55 systems exhibit standard ESR features at 110 K in frozen MeOH with $g_{\perp} = 2.063$ (partially
56
57 resolved hyperfine splitting), $A_{\parallel} = 11$ mT for ^{63,65}Cu, and $g_{\parallel} = 2.25$ ($\mathbf{1}^+$) or 2.32 ($\mathbf{2}^{2+}$),
58
59 respectively. The absorption maxima of the weak ($\epsilon = 400$ M⁻¹ cm⁻¹) d-d transitions lie at 760
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61 nm ($\mathbf{1}^+$) or 690 ($\mathbf{2}^{2+}$), respectively. Both the different charges and the different structural

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3 configurations can account for the spectroscopic variation. Whereas [2](BF₄)₂ containing a
4 labile methanol ligand shows only irreversible reduction, the chloro complex [1]Cl₂ is
5 reversibly reduced at +0.01 V vs ferrocenium/ferrocene in CH₂Cl₂/0.1 M Bu₄NPF₆. This
6 lower number than for the oxidation of copper(I) complexes (see below) indicates the
7 presence of charge compensating chloride.
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17 *Copper(I) compounds*

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22 Although [5](PF₆) could be prepared and studied spectroscopically and electrochemically (cf.
23 below) it could not be crystallized for X-ray structure analysis. We therefore modified the
24 N,Se chelate ligand by methylating the N1 position and using SePh as substituent to yield
25 mpsbi, thus preventing N-H hydrogen bonding. Reaction of mpsbi with [Cu(CH₃CN)₄](PF₆)
26 yielded [3](PF₆), reaction with Cu(BF₄)₂ resulted in copper reduction to yield crystallizing
27 [3](BF₄). The reduction of copper(II) by Cu^I-coordinating organoelement compounds such as
28 phosphines is not uncommon. The structural characterization of [3](BF₄) (Figure 5, Tables
29 1,2) shows a 2+2 coordination pattern [12] as for [Cu(mmb)₂](BF₄), however, with less
30 pronounced straightening of the N-Cu-N angle at 146.7(3)^o vs 169.8(1)^o [6]. The Se system
31 thus approaches a more tetrahedral configuration than the related sulfur species. The remaining
32 bond length and angle parameters are comparable with those of the Cu^I/mmb system [6] and
33 with the copper(II)/Se species described above.
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53 Figure 5

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57 To probe and confirm this S/Se effect we carried out DFT calculations for both species at
58 comparable level. Table 3 shows that the agreement for the Cu coordination environment is
59 good, including particularly the differences in the N-Cu-N angles.
60

Table 3

Due to the larger basis set used the DFT(ADF) optimized geometry of $[\text{Cu}(\text{mmb})_2]^+$ describes better the experimental geometry than the previously published calculations [6]. The substantial features of the experimental structure of $[\text{Cu}(\text{mpsbi})_2](\text{BF}_4)$ (Table 3) are confirmed by the calculations. In particular, the calculation reproduces nicely the experimentally observed lowering of the N-Cu-N angle on going from $[\text{Cu}(\text{mmb})_2]^+$ to the related selenoether complex.

Like for $[\text{Cu}(\text{mmb})_2]^+$, the highest lying molecular orbital of the selenoether complex is mainly formed by a combination of d orbitals from the Cu atom (61%) with p orbitals of the chalcogen (18%). The lowest lying unoccupied molecular orbital is composed from the π^* orbital of the ligand with 11% contribution from the Se atom.

Using the psbi ligand which previously yielded single crystalline Cu^{II} and Ag^{I} complexes [8b] we now managed to obtain not only a BF_4^- salt [8b] but also a hexafluorophosphate compound $[\text{Cu}(\text{psbi})_2](\text{PF}_6)$ which showed a fairly high stability versus oxidation. The single crystals isolated (see Exp. Section) were found to have the composition $[\text{Cu}^{\text{I}}(\text{psbi})_2][\text{Cu}^{\text{I}}(\text{psbi})(\text{psbi}-\text{H}^+)](\text{PF}_6)\cdot\text{CH}_3\text{CN}$ (Figure 6, Tables 1,2). This arrangement follows from the cation/anion ratio 2/1 which thus suggests a partially deprotonation of bound benzimidazole in psbi (3/4 occupancy of N bound H). Such deprotonations have been reported before [18,19], they may be favoured by the presence of the basic heterocycles and by advantageous crystal packing (Figure 7). Supporting this concept, the (averaged) Cu-N bond length is significantly shortened from about 1.94 Å in $[\mathbf{1}]^+$, $[\mathbf{2}]^{2+}$ and $[\mathbf{3}]^+$ (Table 2) to 1.90 Å for $[\mathbf{4}][\mathbf{4}']^+$. In correspondence, the Cu-Se bond distance has increased from about 2.6 Å to 2.85 Å.

Figures 6,7

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8 An additional remarkable feature in [4][4'](PF₆) is the intramolecular Se--Se interaction at
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10 3.6237(3) Å i.e. at lower distance than the sum of the van der Waals radii of ca. 3.8 Å[24].
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12 The attraction is also reflected by the enormously diminished Se-Cu-Se angle of 78.23(4)^o
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14 (Table 2).
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17 The diamagnetic copper(I) compounds exhibit NMR spectra with rather small coordination
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19 induced shifts. Although [4](PF₆) in particular is rather resistant to oxidation, the copper(I)
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21 complexes are converted eventually in air to partly Se-oxygenated products [20].
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24 The reversible oxidation of the copper(I) compounds in CH₂Cl₂/0.1 M Bu₄NPF₆ occurs at
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26 0.29 V ([5]⁺), 0.38 V ([4]⁺) and 0.39 V [3]⁺ vs Fc^{+/0}, reflecting the easier oxidation for the Se-
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28 alkyl instead of the Se-aryl containing system. Nevertheless, the reversibility reflects a rather
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30 small reorganization barrier between the Cu^I and Cu^{II} states [6,11], even with the selenoether
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32 donors present.
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36 **Conclusion.** The metal coordination arrangements of the complex ions described here
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38 illustrate some features distinguishing selenoether from thioether complexes, viz., the
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40 diminished N-Cu^I-N angle as a consequence of relatively stronger Cu^I-Se interaction and the
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42 possibility of Se--Se attraction. Remarkably, the replacement of the SR by the SeR function
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44 resulted in a *less* distorted-tetrahedral structure for copper(I) compounds.
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48 The copper(II) systems are less remarkable, they show the tendency towards linear N-Cu^{II}-
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50 N angles (Table 2) even if the square-pyramidal coordination is not fully achieved. Additional
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52 ligands and the flexibility of the Se donors allow for a considerable structural and
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54 spectroscopic (ESR, UV-vis) variability. Nevertheless, cyclic voltammetric measurements
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56 still exhibit reversible electron transfer Cu^I/Cu^{II}, confirming the suitability also of selenoether
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58 ligands to tolerate both oxidation states.
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Experimental Section

Instrumentation

¹H-NMR spectra were taken on a Bruker AC 250 and 400 spectrometers. EPR spectra were recorded on a Bruker ESP system. UV/Vis absorption spectra were obtained using a J&M Tidas spectrometer. Cyclic voltammetry was carried out in 0.1 M Bu₄NPF₆ solutions using a three-electrode configuration (glassy carbon working electrode, Pt counter electrode, Ag/AgCl reference) and a PAR 273 potentiostat and function generator. The ferrocenium/ferrocene (Fc⁺/Fc) or decamethylferrocenium//decamethylferrocene couples served as internal reference.

Syntheses

2-Methylselenomethyl-1H-benzimidazole (msbi)

A solution of 0.60 g (3.2 mmol) dimethyl diselenide in 15 ml THF is treated with an excess of 1M LiBHEt₃ solution at -10°C. Gas evolution, discolouring and turbidity accompany the reaction. After the gas evolution has ceased 5 ml of EtOH are added for hydrolysis of excess LiBHEt₃. A suspension of 1.2 g (7.23 mmol) of 2-chloromethyl-1H-benzimidazole in 15 ml EtOH is added dropwise and then stirred overnight. After removal of solvent the yellowish ligand is purified by column chromatography on silica 60 with an ethyl acetate/petrol ether (1/1) mixture to yield 26% of the product. Anal Calc. for C₉H₁₀N₂Se (225.15 g/mol): C, 47.86; H, 4.48; N, 12.44%. Found: C, 48.01; H, 4.61; N, 12.17%. ¹H-NMR (CD₃CN): 2.04 (s, CH₃), 3.93 (s, CH₂), *J*(CH-⁷⁷Se 6.9 Hz); 7.15-7.25 (m, CH), 7.45-7.55 (m, CH). ¹³C-NMR (CD₃CN): 4.8 (CH₃), 19.7 (CH₂), *J*(¹³C-⁷⁷Se 30 Hz); 115.7, 123.2, 139.3, 154.6. ⁷⁷Se-NMR (CD₃CN): 155.

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1-Methyl-2-phenylselenomethyl-1H-benzimidazole (mpsbi)

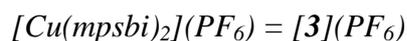
A mixture of 0.73 g (6.0 mmol) freshly distilled N-methyl-*o*-phenylenediamine and 1.31 g (6.1 mmol) of 2-phenylselenoacetic acid was heated to reflux for 20 h in 25 ml of half concentrated hydrochloric acid. After removal of the excess hydrochloric acid under vacuum the residue was suspended in 25 ml H₂O and added slowly to 25 ml of cold concentrated ammonia solution. The dark oil formed was extracted several times with dichloromethane. Drying with Na₂SO₄ and removal of CH₂Cl₂ yielded a brown solid which was dissolved in ethyl acetate. After filtering the solution and adding a few drops of triethylamine the mixture was chromatographed on a silica column (ethyl acetate/petrol ether 80/20) to yield a light brown oil which solidified at 0°C. Recrystallization from ethyl acetate yielded the light brownish product in 47% yield (0.84 g). Anal Calc. for C₁₅H₁₄N₂Se (301.24 g/mol): C, 59.81; H, 4.68; N, 9.30%. Found: C, 59.90; H, 4.72; N, 9.25%. ¹H-NMR (CDCl₃): 3.56 (s, CH₃), 4.31 (s, CH₂), 7.15-7.70 (m, CH). ¹³C-NMR (CDCl₃): 22.6 (CH₂), 30.5 (CH₃), 109.5, 119.9, 122.6, 123.1, 128.5, 129.6, 134.5, 134.6, 136.0, 143.3, 150.5. ⁷⁷Se-NMR (CDCl₃): 937. The compound was alternatively obtained by reacting the corresponding 1-methyl-2-chloromethyl-1H-benzimidazole with PhSe⁻ [8b].

[Cu(msbi)₂Cl]Cl·2 MeOH = [1](Cl)·2 MeOH

100 mg (0.44 mmol) of msbi and 30 mg (0.22 mmol) of CuCl₂ were dissolved in 10 ml CH₃OH by gentle heating. Slow cooling yielded greenish crystals in 87% yield (112 mg). Anal Calc. for C₂₀H₂₈Cl₂CuN₄O₂Se₂ (648.82 g/mol): C, 37.02; H, 4.13; N, 8.64%. Found: C, 36.10; H, 4.35; N, 8.73%.

[Cu(msbi)₂(MeOH)](BF₄)₂ = [2](BF₄)₂

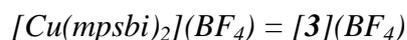
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3 100 mg (0.44 mmol) of msbi and 52 mg (0.22 mmol) of Cu(BF₄)₂ were dissolved in 2 ml
4
5 CH₃OH. Layering with 10 ml diethyl ether and cooling to -18°C yielded green crystals in 35%
6
7 yield (56 mg). Anal Calc. for C₁₉H₂₄B₂CuF₈N₄OSe₂ (719.50 g/mol): C, 31.72; H, 3.36; N,
8
9 7.79%. Found: C, 31.45; H, 3.62; N, 7.60%.



16
17 The precursor compound [Cu(CH₃CN)₄](PF₆) (50 mg, 0.134 mmol) and the ligand mpsbi (81
18
19 mg, 0.268 mmol) were mixed under argon in 10 ml CH₃CN, stirred for 2 hours, and the
20
21 solvent was slowly removed to yield 72 mg (66%) of the sensitive product. Anal Calc. for
22
23 C₃₀H₂₈CuF₆N₄PSe₂ (811.01 g/mol): C, 44.43; H, 3.48; N, 6.91%. Found: C, 43.94; H, 3.25; N,
24
25 7.05%. ¹H-NMR (CD₃CN): 3.73 (s, CH₃), 4.42 (s, CH₂), *J*(CH₂-⁷⁷Se 6.9 Hz); 7.14-7.58 (m,
26
27 CH). ¹³C-NMR (CD₃CN): 23.4 (CH₂), *J*(¹³C-⁷⁷Se 30 Hz); 30.5 (CH₃), 110.7, 118.1, 123.1,
28
29 123.6, 128.2, 128.6, 129.2, 129.4, 129.6, 135.9, 155.2. ⁷⁷Se-NMR (CD₃CN): 309.



37
38 The precursor [Cu(CH₃CN)₄](PF₆) (50 mg, 0.134 mmol) and the ligand msbi (60 mg, 0.268
39
40 mmol) were stirred in 10 ml CH₃CN for 2 hours, and the solvent was slowly removed to yield
41
42 68 mg (72%) of the very sensitive product. Anal Calc. for C₁₈H₂₀CuF₆N₄PSe₂ (658.81 g/mol):
43
44 C, 32.82; H, 3.06; N, 8.51%. Found: C, 32.78; H, 2.97; N, 9.10%. ¹H-NMR (CD₃CN): 2.11 (s,
45
46 CH₃), 4.05 (s, CH₂); 7.28-7.62 (m, CH). ¹³C-NMR (CD₃CN): 6.3 (CH₃), 21.3 (CH₂), 30.5
47
48 (CH₃), 115.1, 123.1, 129.7, 154.8.



56
57 A solution of 83 mg (0.28 mmol) of mpsbi in 3 ml MeOH was treated with a solution of 48
58
59 mg (0.14 mmol) of Cu(BF₄)₂·6 H₂O in 3 ml methanol. The dark-green solution was stirred for
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one day, the solvent volume reduced to 50% and a green solid precipitated by cooling to 4°C.

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3 Redissolving in dry MeOH and keeping at 4°C produced 12 mg (11 %) of colorless crystals
4
5 (rods) suitable for X-ray diffraction. ¹H-NMR (CDCl₃): 3.71 (s, CH₃), 4.45 (s, CH₂), 7.15-
6
7 7.70 (m, CH).
8
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15 The precursor compound [Cu(CH₃CN)₄](PF₆) (50 mg, 0.134 mmol) and the ligand psbi (77
16 mg, 0.268 mmol) were mixed under argon in 10 ml CH₃CN, stirred for 2 hours, and the
17 solvent was slowly removed to yield 87 mg (83%) of the product. Anal. Calc. for
18 C₂₈H₂₄CuF₆N₄PSe₂ (782.95 g/mol): C, 42.95; H, 3.09; N, 7.16%. Found: C, 42.56; H, 3.45; N,
19 6.86%. ¹H-NMR (CD₃CN): 4.39 (s, CH₂), 7.18-7.60 (m, CH). ¹³C-NMR (CD₃CN): 26.0,
20 117.8, 124.4, 129.0, 129.6, 130.0, 133.5, 163.5, 186.0. Crystallization at -18°C of an
21 acetonitrile solution produced single crystals of [Cu^I(psbi)₂][Cu^I(psbi)(psbi-H⁺)](PF₆)·CH₃CN
22 = [4][4'](PF₆)·CH₃CN. Anal. Calc. for C₅₈H₅₀Cu₂F₆N₉PSe₄ (1462.901 g/mol): C, 47.68; H,
23 3.45; N, 8.63%. Found: C, 47.58; H, 3.54; N, 8.66%.
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39 *Crystal Structure Determination*

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43 Colorless single crystals of [3](BF₄) were obtained from a methanol solution at 4°C.
44 Green single crystals of [2](BF₄)₂ were grown by slow diffusion of diethyl ether into a
45 methanol solution. Data for both crystals were collected at 293 K with a NONIUS Kappa
46 CCD diffractometer. Green single crystals of [1]Cl·2 MeOH were obtained by slow
47 evaporation from a saturated methanol solution, single crystals of [4][4'](PF₆)·CH₃CN were
48 obtained from a concentrated acetonitrile solution, and single crystals of msbi were grown
49 from an ethyl acetate/petrol ether (1/1) mixture by slow evaporation at room temperature.
50 Data collection for these crystals was performed at 173 K (msbi, [4][4'](PF₆)·CH₃CN) and
51 293 K ([1]Cl·2 MeOH) on a Siemens P4 diffractometer employing the ω–2θ scan technique.
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3 The structures were solved by direct methods using the SHELXTL package [25], and
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5 refinement was carried out with SHELXL97 employing full matrix least-squares methods on
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7 F^2 with $F_o^2 \geq 2\sigma(F_o^2)$. All non-hydrogen atoms were treated anisotropically; hydrogen atoms
8
9 were included by using appropriate riding models. Additional crystallographic information is
10
11 given in Table 1.
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13

14
15 Crystallographic data have been deposited with the Cambridge Crystallographic Data
16
17 Centre, CCDC-722404 - CCDC-722408. Copies of the information may be obtained free of
18
19 charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)
20
21 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk; www: <http://www.ccdc.cam.ac.uk>).
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27 *DFT Calculations*

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32 Ground state electronic structure calculations of the complex ions $[\text{Cu}(\text{mmb})_2]^+$ and
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34 $[\text{Cu}(\text{mpsbi})_2]^+$ have been done by the density-functional theory (DFT) method using
35
36 ADF2007.1 [26-28]. Slater type orbital (STO) basis sets of triple- ζ quality with two
37
38 polarization functions for S, Se and Cu and triple- ζ quality with one polarization function for
39
40 the other atoms were employed. The inner shells were represented by the frozen core
41
42 approximation (1s for C, N, 2p for S, 3p for Se and 1s-2p for Cu were kept frozen). The
43
44 following density functionals were used within ADF: The local density approximation (LDA)
45
46 with VWN parametrization of electron gas data or the functional including Becke's gradient
47
48 correction [29] to the local exchange expression in conjunction with Perdew's gradient
49
50 correction [30] to the LDA expression (ADF/BP). The scalar relativistic (SR) zero order
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52 regular approximation (ZORA) was used within this study. Geometry optimizations were
53
54 done without any symmetry constraints.
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3 This work was supported by the Deutsche Forschungsgemeinschaft (SFB 706), the Fonds
4 der Chemischen Industrie, the EU (COST D35), the Grant Agency of the Academy of
5
6 Sciences of the Czech Republic (KAN 100400702) and the Ministry of Education of the
7
8 Czech Republic (Grant COST OC 139).
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Table 1. Crystal and refinement data for ligand and complexes

	msbi	[1](Cl) \cdot 2 MeOH	[2](BF ₄) ₂	[3](BF ₄)	[4][4'](PF ₆) \cdot CH ₃ CN
empirical formula	C ₉ H ₁₀ N ₂ Se	C ₂₀ H ₂₈ Cl ₂ CuN ₄ O ₂ Se ₂	C ₁₉ H ₂₄ B ₂ CuF ₈ N ₄ OSe ₂	C ₃₀ H ₂₈ BCuF ₄ N ₄ Se ₂	C ₅₈ H ₅₀ Cu ₂ F ₆ N ₉ PSe ₄
molar mass	225.15	648.82	719.52	752.83	1460.96
temperature (K)	173(2)	293(2)	293(2)	293(2) K	173(2) K
wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	tetragonal
space group	<i>Pbca</i>	<i>C2/c</i>	<i>C2/c</i>	<i>C2/m</i>	<i>P4/n</i>
cell dimensions (Å)	<i>a</i> = 8.7058(9)	<i>a</i> = 17.516(4)	<i>a</i> = 21.4292(5)	<i>a</i> = 20.6470(7)	<i>a</i> = 13.6880(19)
	<i>b</i> = 9.7525(11)	<i>b</i> = 11.667(2)	<i>b</i> = 17.6223(4)	<i>b</i> = 6.5126(3)	<i>b</i> = 13.6880(19)
	<i>c</i> = 21.747(2)	<i>c</i> = 12.566(3)	<i>c</i> = 16.4925(4)	<i>c</i> = 12.6499(6)	<i>c</i> = 15.174(3)
		β = 105.75(3) $^\circ$	β = 121.096(1) $^\circ$	β = 116.030(2) $^\circ$	
cell volume (Å ³)	1846.4(3)	2471.6(9)	5333.1(2)	1528.44(11)	2843.0(8)
Z	8	4	8	2	2
calc. density (Mg/m ³)	1.620	1.744	1.737	1.636	1.707
absorption coefficient (mm ⁻¹)	4.012	4.070	3.625	3.147	3.404

F(000)	896	1292	2808	748	1448
measured Θ region ($^{\circ}$)	1.87-26.99	1.06-29.00	1.02-28.28	3.28 - 24.69	1.085 – 29.00
index region	$-1 \leq h \leq 11$	$-22 \leq h \leq 23$	$-28 \leq h \leq 28$	$-24 \leq h \leq 24$	$-17 \leq h \leq 17$
	$-1 \leq k \leq 12$	$-15 \leq k \leq 0$	$-23 \leq k \leq 23$	$-7 \leq k \leq 6$	$-17 \leq k \leq 17$
	$-1 \leq l \leq 27$	$-17 \leq l \leq 0$	$-21 \leq l \leq 21$	$-14 \leq l \leq 14$	$-19 \leq l \leq 19$
no of reflections	2013	3281	6597	6867	3225
no of independent reflections	1441 [$R_{\text{int}} =$ 0.0478]	2780 [$R_{\text{int}} = 0.0269$]	3268 [$R_{\text{int}} = 0.0607$]	2360 [$R_{\text{int}} = 0.0564$]	2383 [$R_{\text{int}} = 0.1700$]
absorption correction	PSI scan	PSI scan	empirical	numerical (HABITUS)	PSI scan
data/restraints/parameters	2013 / 0 / 117	3281 / 0 / 198	6597 / 0 / 334	6867 / 1 / 199	3225/0/186
goodness-of-fit on F^2	1.170	1.256	1.062	0.906	1.087
final R values [$I > 2\sigma(I)$]	R1 = 0.0460,	R1 = 0.0336,	R1 = 0.0755,	R1 = 0.0422,	R ₁ = 0.0662
	wR2 = 0.0978	wR2 = 0.0727	wR2 = 0.1971	wR2 = 0.1156	wR ₂ = 0.1413
R values (all data)	R1 = 0.0769,	R1 = 0.0460, wR2 =	R1 = 0.0858, wR2 =	R1 = 0.0513,	R ₁ = 0.0946
	wR2 = 0.1099	0.0771	0.2047	wR2 = 0.1245	wR ₂ = 0.1645

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3 max/min electron density ($\text{e}\text{\AA}^{-3}$) 0.473; -0.508 0.661; -0.562 4.002; -1.360 0.41; -0.27 0.164; -1.20
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Table 2 Selected bond parameters

compound	Cu-N	Cu-Se	N-Cu-N	Se-Cu-Se	Se-Cu-N
[1]Cl·2 MeOH	1.944(2)	2.6205(6)	169.17(12)	133.75(2)	82.60(6); 93.13(6)
[2](BF ₄) ₂	1.933(5)	2.532(1)	171.2(2)	150.60(4)	83.4(2); 94.8(2)
	1.947(5)	2.552(1)			82.7(2); 95.1(2)
[3](BF ₄)	1.948(5)	2.632(1)	146.7(3)	110.91(6)	84.1(2); 115.4(2)
[4 [*]](PF ₆)·CH ₃ CN	1.898(5)	2.849(1)	157.5(3)	78.23(4)	81.9(2); 116.4(2)

Table 3. Comparison of Selected Experimental and Calculated Bond Lengths [\AA] and Angles [$^\circ$] within $[\text{Cu}(\text{mpsbi})_2](\text{BF}_4)$ and $[\text{Cu}(\text{mmb})_2](\text{BF}_4)$.

Bond length	X=Se (L = mpsbi)		X=S (L = mmb)	
	exp.	calc.	exp.	calc.
	(this work)	(this work)	[6]	(this work)
Cu-N(1)	1.948(5)	1.928	1.9199(18)	1.918
Cu-X	2.632(1)	2.636	2.6216(7)	2.702
X-C(9)	1.925(4)	1.982	1.801(3)	1.824
X-C(10)	1.914(5)	1.947	1.806(3)	1.826
Bond angle				
N(1)#1-Cu-N(1)	146.7(3)	146.3	169.75(11)	166.6
N(1)#1-Cu-X	115.35(15)	114.0	103.56(6)	106.9
N(1)-Cu-X	84.09(15)	86.0	82.47(6)	81.8
X-Cu-X#1	110.91(6)	109.1	109.33(3)	112.2
C(9)-X-Cu	90.47(12)	88.4	90.42(9)	89.7
C(10)-X-Cu	93.98(13)	96.1	93.7(1)	93.2
C(10)-X-C(9)	101.1(2)	100.3	100.7(1)	101.1
C(8)-N(1)-C(6)	104.5(5)	106.5	105.5(2)	106.4
C(8)-N(1)-Cu	123.6(4)	120.6	120.8(2)	120.6
C(6)-N(1)-Cu	131.4(4)	130.4	132.4(2)	131.1

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3 **Figure captions**
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5
6 **Fig. 1** Molecular structure of msbi in the crystal (C10-Se 1.960(4) Å, Se-C11 1.934(5) Å,
7
8 C10-Se-C11 97.1(2)°, C2-C10-Se-C11 66.0°).
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13 **Fig. 2** Molecular structures of cation 1^+ and solvated anion in the crystal of $[1]Cl \cdot 2 MeOH$.
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18 **Fig. 3** Molecular structure of 2^{2+} in the crystal of $[2](BF_4)_2$.
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21
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23 **Fig. 4** Coordination figures at the metal centers in the complex ions 1^+ (left) and 2^{2+} (right).
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26
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28 **Fig. 5** Molecular structure of cation 3^+ in the crystal of $[3](BF_4)$.
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33 **Fig. 6** Molecular structure of averaged complexes in the crystal of $[4][4'](PF_6) \cdot CH_3CN$.
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37 **Fig. 7** Packing in the unit cell of single crystalline $[4][4'](PF_6) \cdot CH_3CN$.
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42 **Fig. 8** Coordination arrangement in $[Cu(mpsbi)_2]^+$ (top) and $[Cu(mmb)_2]^+$ (bottom).
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Figure 1

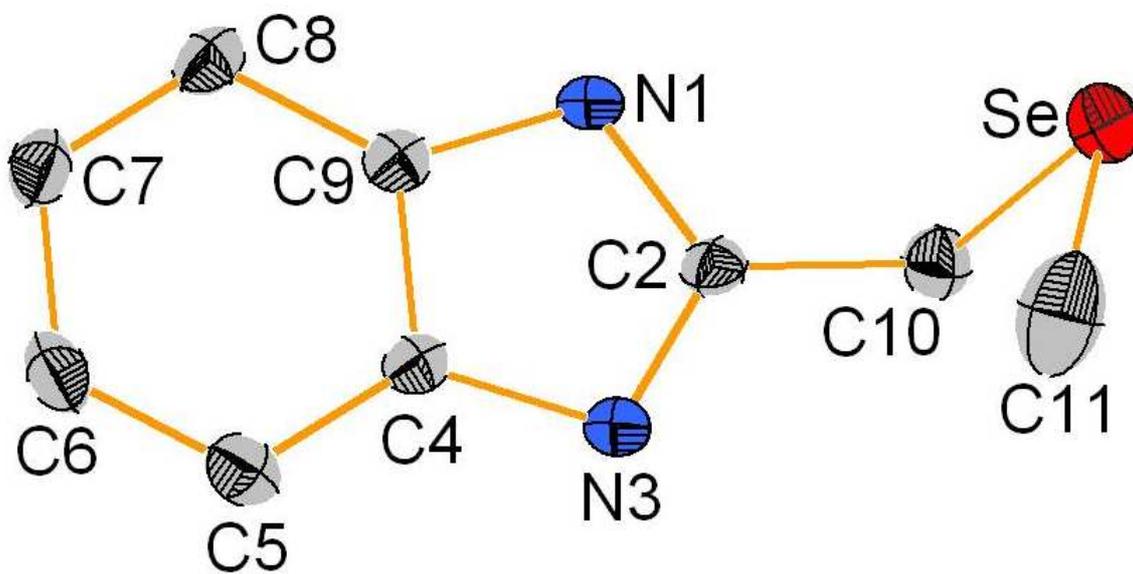


Figure 2

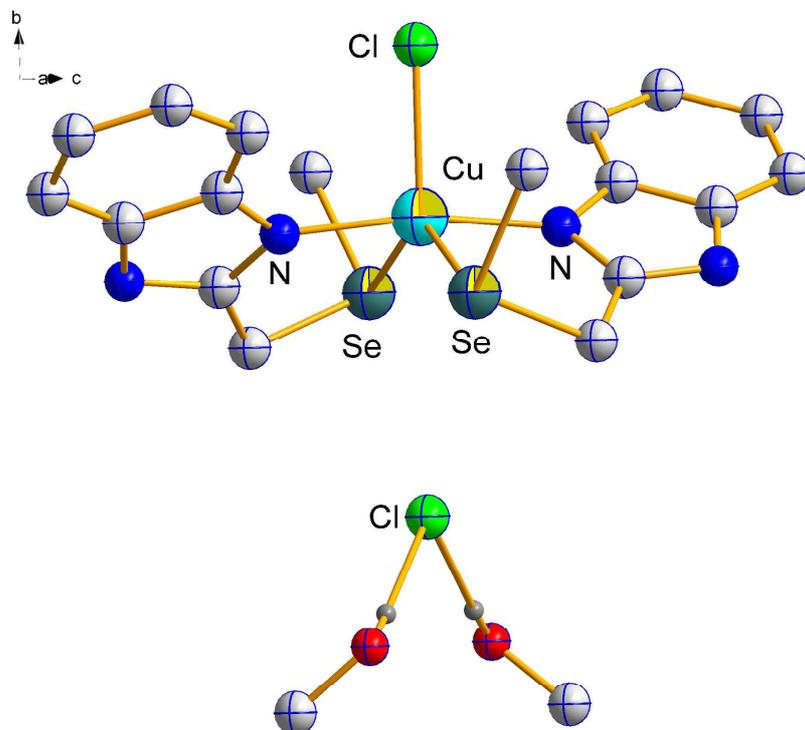


Figure 3

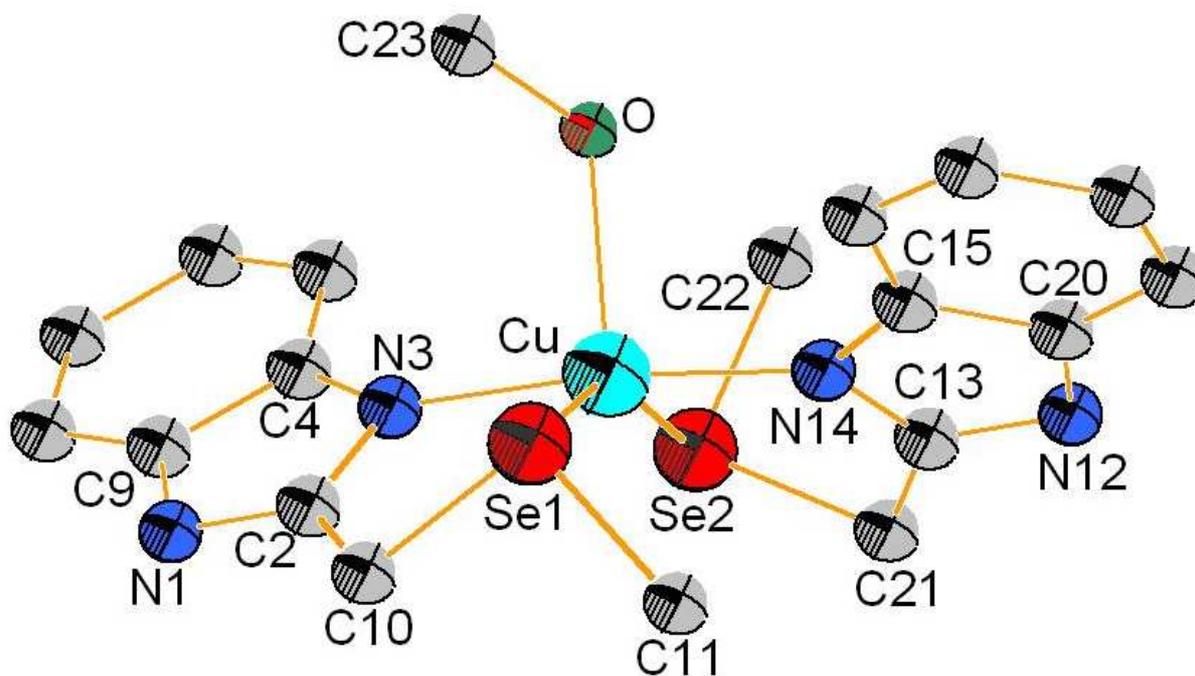


Figure 4

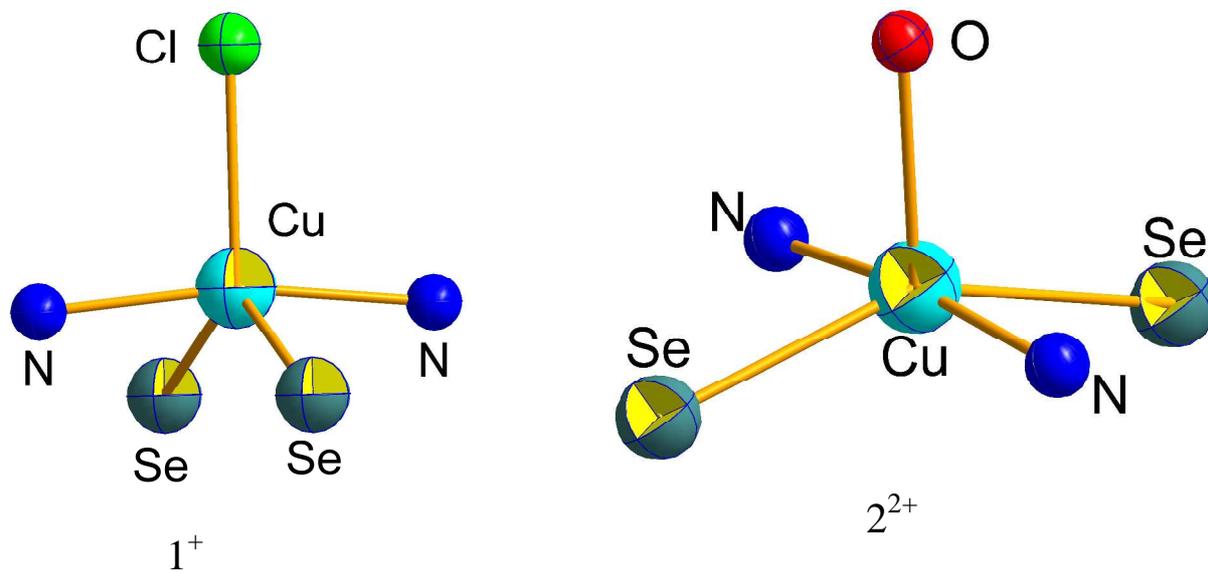


Figure 5

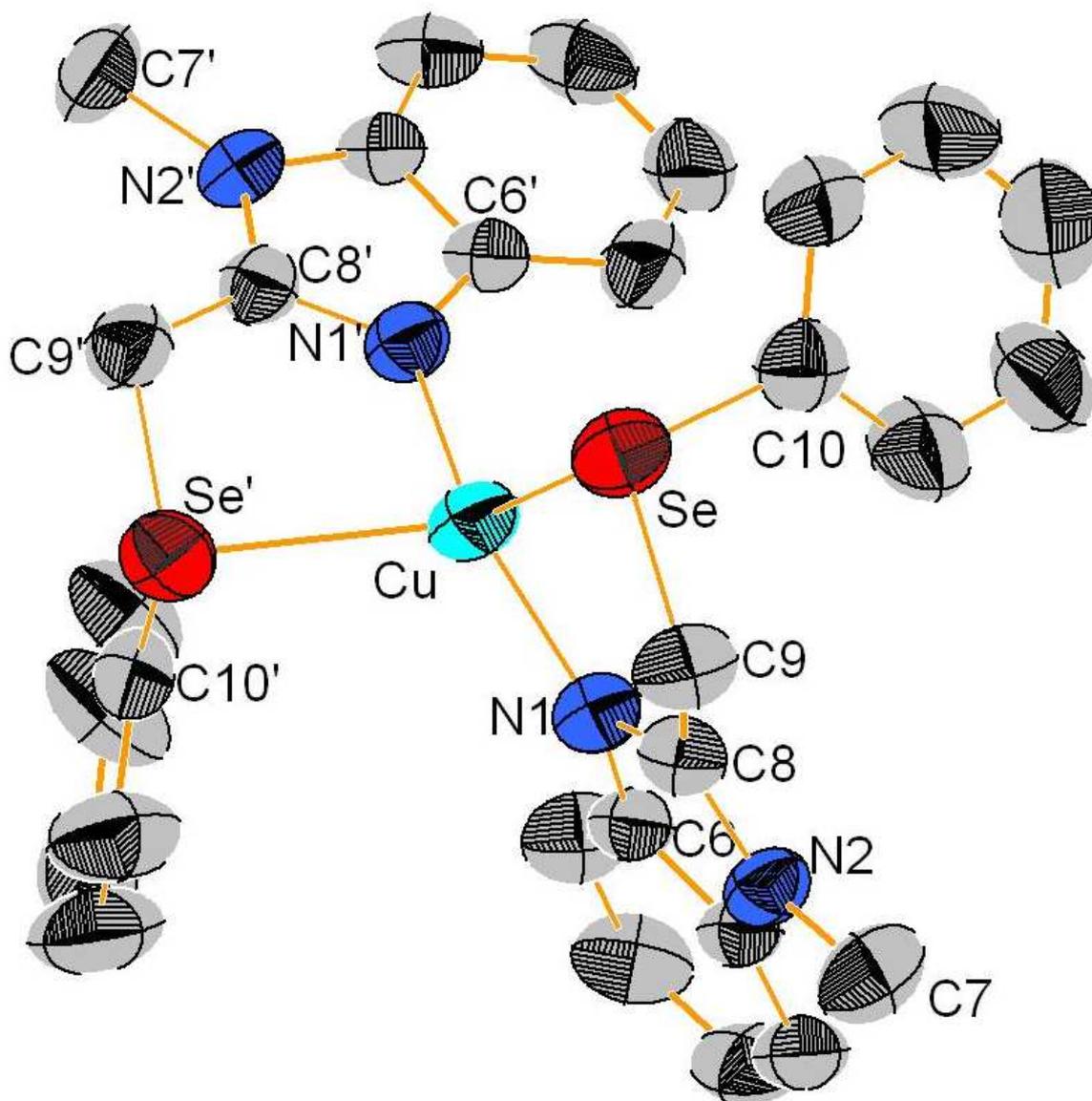


Figure 6

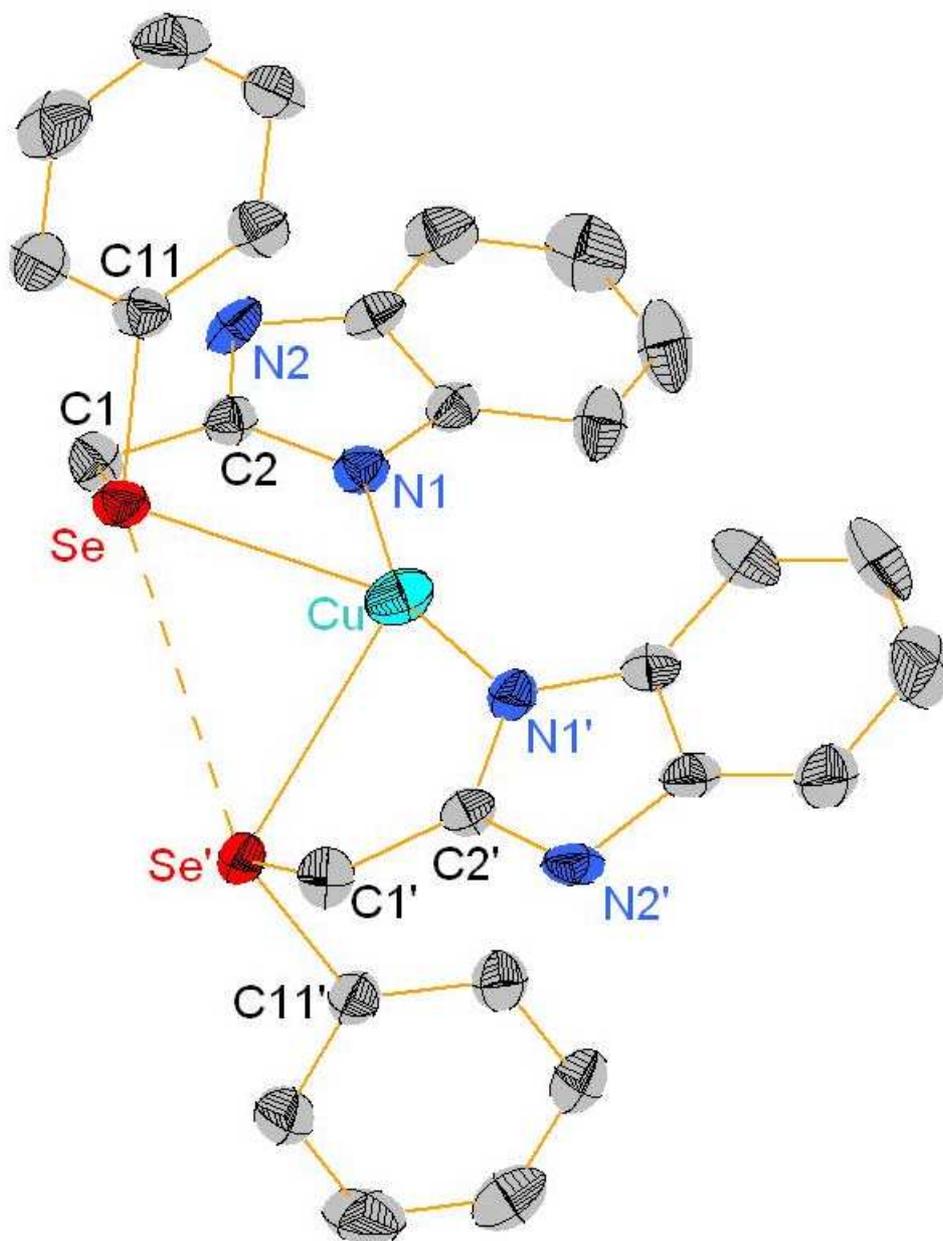


Figure 7

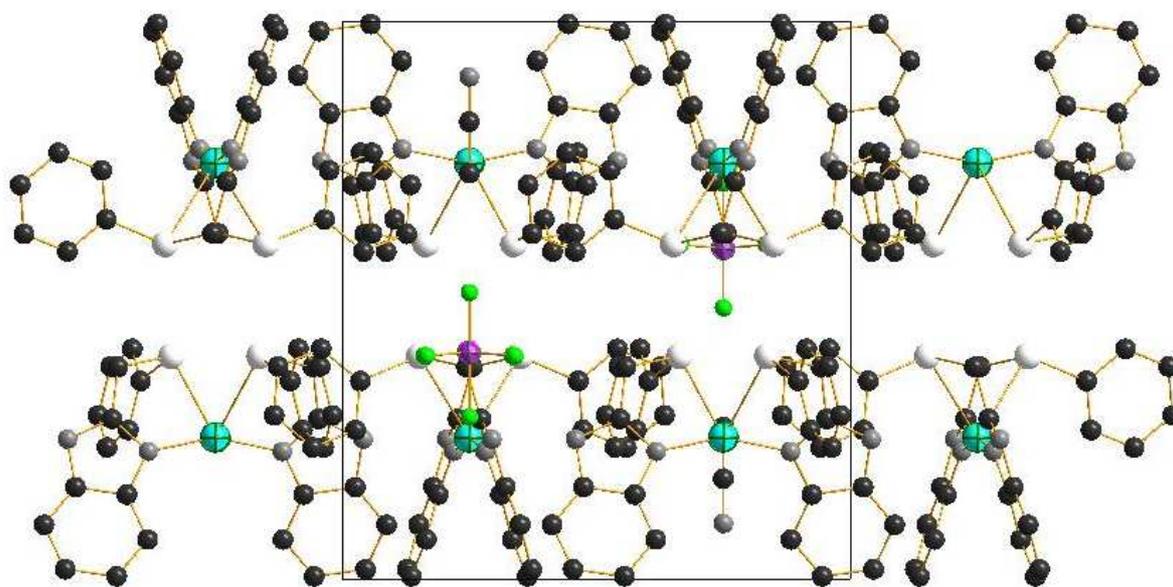


Figure 8

