Synthesis, characterization, and DFT studies of thione and selone Cu(I) complexes with variable coordination geometries†

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Coordination of Cu(I) halides with N,N’-dimethylimidazole selone (dmise) and thione (dmit) ligands was examined by treating CuX (X = Cl, Br, I) with one or two equivalents of dmise or dmit. The reaction of Cu and CuBr with one molar equivalent of dmise results in unusual selenium-bridged tetrameric Cu4(dmise)4(μ-X)4 core (X = Cl, Br, I) with two equivalents of dmise or dmit results in trigonal planar Cu(I) complexes of two different conformations with the formula Cu(dmise)3X3 (3a, 3b, 4, and 7) or Cu(dmit)X2 (2, 5, and 8) with average Cu–S and Cu–Se bond lengths of 2.23 Å and 2.34 Å, respectively. The coordination geometry around the copper center in complexes 1 to 8 is determined by the type of halide and chalcogenone ligand used, intramolecular π–π interactions, and short contact interactions between X–H (X = I, Br, Cl, Se or S). The theoretical DFT calculations are in good agreement with experimental X-ray structural data and indicate that dmise ligands are required for formation of the tetrameric complexes 1 and 6. Electrochemical studies show that the trigonal copper selone complexes have more negative potentials relative to analogous copper thione complexes by an average of 108 mV.

Introduction

There is increased interest in the chemistry of copper with soft Lewis base donors such as thiolates, thioamides, selenolates and selenolamines for use in catalysis1 and in bioinorganic chemistry for the study of copper metallothioneins and metallochaperones.2–5 Of particular interest is the coordination chemistry of selenium with biologically-important transition metals (Cu, Fe, Ni, Zn, Mn, Mo, etc.), since selenium has been shown to possess stronger antioxidant activity.6–8 Our group has determined that copper coordination to sulfur and selenium containing ligands is a novel mechanism for selenium and sulfur antioxidant activity.9,10 We are interested in the chemistry of N,N’-dimethylimidazole selone (dmise) and thione (dmit) (Fig. 1) because these and similar ligands are effective antioxidants.14,15

The dmise and dmit ligands are similar to methimazole, a drug currently used in the treatment of hyperthyroidism,16 and also resemble ergothioneine17,18 and selenoneine,19 sulfur- and selenium-containing antioxidants naturally found in plants and animals.

† Electronic supplementary information (ESI) available: Crystal packing diagrams (Fig. S1–S2), XRD powder patterns (Fig. S3–S12), cyclic voltammograms (Fig. S13), DPV voltammograms (Fig. S14–S15), CCDC reference numbers 804911–804919. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10104h
(Y = Cl, Br; L = N,N′-dimethylimidazolidine selone), and Cu₂(btseme)X₂ (X = Cl, Br, NO₃, SO₄; btseme = N-methylbenzothiazole-2-selone).

This work reports the synthesis of copper halide complexes with dmise and dmit ligands, with the aim of studying their different coordination modes and electrochemistry. Complexes of the formulas Cu₄(μ-L₄)(μ-X₂)X₂, CuL₂X, CuL₂X₂, CuL₂Y and CuL₂X₂ (L = dmise, L’ = dmit; X = I, Br; Y = Cl) have been synthesized and characterized using ¹H, ¹³C{¹H} and 77Se{¹H} NMR spectroscopy, cyclic voltammetry, X-ray structural analysis, X-ray powder diffraction (XRD), and electrospray ionization mass spectrometry (ESI-MS). Observed differences in the coordination geometries and packing orientations of these complexes are also examined using density functional theory (DFT) calculations.

Results and discussion

Synthesis of Cu(I)-chalcogenone halide complexes

The target metal complexes were synthesized by treating copper halides with one or two molar equivalents of selone or thione. The reaction of CuI and CuBr with one molar equivalent of dmise resulted in formation of tetranuclear copper complexes with bridging selone ligands (1 and 6; Fig. 2A). The tetranuclear copper-iodide-selone complex (1) can also be synthesized via a two-step, one-pot reaction with molar equivalents of [Cu(NCCH₃)₄][BF₄] and dmise in acetonitrile, resulting in an insoluble precipitate that is redissolved by addition of KI in methanol, similar to a method previously described by Niu, et al.⁴⁵ Both synthetic methods result in similar yields of 1.

Treating CuI with two molar equivalents of dmise or dmit in acetonitrile and dichloromethane results in the formation of monomeric three-coordinate copper-iodo complexes (2 and 3a) characterized by intramolecular π–π interactions between the two heterocyclic five-membered rings (Fig. 2B). In contrast, treating two molar equivalents of dmit with CuI in a mixed solvent system of ethanol and dichloromethane results in the formation of a trigonal copper complex (3b) with no intramolecular π–π interactions (Fig. 2C).

The three-coordinate copper chloride or bromide complexes (4, 5, 7, and 8) are synthesized by treating two molar equivalents of dmit or dmise with CuCl or CuBr in a mixed solvent system (Fig. 2C). The X-ray crystal structure of Cu(dmit)₂Cl has been reported by Kim, et al. but its synthesis and characterization was not reported.¹ The trigonal copper complexes (2, 3a, 3b, 4, 5, 7 and 8) can be synthesized with good yields (85–92%), whereas the tetrameric complexes 1 and 6 have an average yield of 23%. Crystals of the target metal complexes are stable in air but the Cu⁺ ions are easily oxidized to Cu²⁺ in solution.

Crystallographic studies of Cu(I) halides with heterocyclic selone and thione ligands

The X-ray crystal structures of Cu₄(μ-dmise)(μ-I)₂I₂ (1) and Cu₄(μ-dmise)(μ-Br)Br₂·0.5CH₃CN (6) show two different coordination geometries around the copper ions (Fig. 3; bond distances and angles in Table 1). Two selenium atoms and one iodide or bromide ion each coordinate the Cu(2) and Cu(2A) ions in a distorted trigonal planar geometry. Trigonal copper bond angles range from 116.11(3)° to 121.81(6)° in 1 and from 119.56(3)° to 119.71(5)° for the less distorted trigonal copper

Fig. 2 Synthetic procedures for the preparation of tetrameric and trigonal planar copper complexes.
Table 1 Experimental crystal data (EXP) vs. theoretical DFT calculations for selected bond lengths and angles of Cu₄(µ-dmise)₄(µ-I)₂I₂ (1) and Cu₄(µ-dmise)(µ-Br)₂Br₂ (6)

<table>
<thead>
<tr>
<th></th>
<th>X = I; Y = Se (EXP)</th>
<th>X = I; Y = Se (DFT)</th>
<th>X = Br; Y = Se (EXP)</th>
<th>X = Br; Y = Se (DFT)</th>
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<td>Cu(1)–Y</td>
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<td>2.470</td>
<td>2.4087(7)</td>
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<td>Cu(1)–X(1)</td>
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<td>2.731</td>
<td>2.582</td>
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<tr>
<td>Cu(1)–Cu(1A)</td>
<td>2.607(2)</td>
<td>2.591</td>
<td>2.630</td>
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<tr>
<td>Cu(2)–Y(2)</td>
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<td>2.4130(8)</td>
<td>2.434</td>
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<tr>
<td>Cu(2)–X(2)</td>
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<td>2.566</td>
<td>2.4298(13)</td>
<td>2.382</td>
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<tr>
<td>Cu(2)–X(1)</td>
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<td>3.492</td>
<td>3.428</td>
<td>3.763</td>
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<td>Y–Cu(2)–Y</td>
<td>121.81(6)</td>
<td>119.9</td>
<td>119.71(5)</td>
<td>118.3</td>
</tr>
<tr>
<td>Y–Cu(2)–X(2)</td>
<td>116.11(3)</td>
<td>118.7</td>
<td>119.56(3)</td>
<td>120.7</td>
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<td>Y–C(1)</td>
<td>1.882(5)</td>
<td>1.904</td>
<td>1.900</td>
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</table>

Fig. 3 X-ray crystal structure diagrams of Cu₄(µ-dmise)(µ-I)₂I₂ (1; left) and Cu₄(µ-dmise)(µ-Br)₂Br₂ (6; right) showing 50% probability density ellipsoids. Hydrogen atoms are omitted for clarity.

centers in 6. Cu–I and Cu–Br bond distances are 2.58 Å and 2.43 Å, respectively, for 1 and 6, and the Cu–Se bond distances are 2.42 Å and 2.41 Å, respectively.

The two additional copper centers (Cu(1) and Cu(1A)) in 1 and 6 adopt distorted tetrahedral geometries with a Cu₂(µ-I) or Cu₂(µ-Br) core (average Cu–Cu distance 2.62 Å) and two bridging selenium atoms from the dmise ligand. Each Cu⁺ ion in the core has distorted tetrahedral geometry with angles about each copper varying from 89.6 to 140.7° in 1 and 90.3° to 142.7° in 6. The central Cu₂(µ-I) core in 1 is rhomboidal with bridging Cu–I bond distances of 2.76 Å, longer than the terminal Cu–I bond distances of 2.58 Å. The angles in the Cu₂(µ-I) core are 56.3° for I(1)–Cu(I)–(1A) and 123.7° for Cu(I)–I(1)–Cu(1A), whereas the Cu₂(µ-Br) core in 6 has Br(1)–Cu(1)–Br(1A) and Cu(1)–Br(1)–Cu(1A) angles of 50.6° and 104.2°, respectively. The tetrameric complex 6 has bridging Cu–Br bond distances of 2.65 Å, longer than the terminal Cu–Br bond distances of 2.43 Å. In the X-ray structures of 1 and 6, the average Cu–Se bond lengths of 2.41 Å are shorter or comparable to most reported bridging copper-selenium complexes in the literature46–48 but longer than previously synthesized mononuclear copper-selone complexes such as [Tpm*Cu(dmise)]⁺ (2.30 Å) and Tp*Cu(dmise) (2.33 Å).49

The bond distances for Cu(I)–I(1) (2.76 Å), Cu(2)–I(2) (2.58 Å), Cu(1)–Br(1) (2.65 Å) and Cu(2)–Br(2) (2.43 Å) are shorter than the sum of the ionic radii of Cu⁺ and I⁻ (2.97 Å) and Cu⁺ and Br⁻ (2.73 Å), respectively.49

Short-contact interactions between iodine and hydrogen atoms are observed in the packing diagram of complex 1 (supplementary information, Fig. S1†), whereas the packing diagram of complex 6 shows no short-contact interactions. Short contact interactions of 3.16 Å between I(2)-H₂B in 1 are within the sum of their van der Waals radii (3.18 Å) and possibly promote stability of this complex. The long Cu(1)–Cu(1A) distances in 1 and 6 indicate little interaction between these ions.

The DFT(B3PW91) structures of the tetrameric complexes 1 and 6 were optimized in C₂ᵥ symmetry and are in good agreement with X-ray crystallographic data (Table I). Bond distances and angles generally within 0.04 Å and 2° of experimental values with the exception of the Cu(2)–X(1) short contact which is underestimated by 0.25–0.35 Å. Slight overestimation of the calculated X-H₂B short contacts may be attributed to the absence of intermolecular X–H interactions in the gas phase. The DFT(B3PW91)-optimized
geometries of the hypothetical thione analogs (1(S) and 6(S)) were similar to 1 and 6 with shorter Cu–Y bond distances. The energies of formation (ΔE+ZPE) of these species relative to the CuX(dmit/dmise) monomers were ~10 kcal mol⁻¹ less favorable than for 1 and 6.

Treating copper halide compounds with two equivalents of dmit or dmsi results in the formation of monomeric three-coordinate complexes with differing geometries. The molecular structures and atom numbering schemes for Cu(dmise)₂I(2), trans-Cu(dmit)₂I(3a), and Cu(dmise)₂Br(8) are given in Fig. 4, and Table 2 lists their selected bond distances and angles. X-ray structural studies established that these complexes are monomeric with two non-bridging selone and thione ligands coordinated to copper. The heterocyclic rings in complexes 2, 3a, and 8 adopt a trans conformation relative to the halogen atom along the copper-chalcogenone bond. The Cu⁺ ion has distorted trigonal geometry with angles ranging from 111.56° to 136.87° for 2; 111.82° to 136.87° for 3a; and 108.0° to 144.0° for 8. The Cu–Se and Cu–S bond distances are 2.34 Å for 2 and 3a and 2.23 Å for 8, whereas the Cu–I bond distances in 2 and 3a are approximately 2.56 Å. Short contact interactions between iodine and hydrogen atoms are found within the unit cell of trans-Cu(dmit)₂I(3a; supplementary information, Fig. S2†) but are absent in the unit cell of the selenium analog Cu(dmise)₂I(2). The short contact interaction of 3.18 Å between I and H5C is equal to the sum of their van der Waals radii (3.18 Å).

Relatively short distances between the selone heterocyclic ligands ranging from 3.63 Å (A) to 3.95 Å (B) are observed for 2 (Fig. 5), whereas distances of 3.67 Å (A) to 3.90 Å (B) are observed between the two heterocyclic thione ligands in complex 3a, indicating intramolecular π–π interactions are present in both. In contrast, complex 8 exhibits no intramolecular π–π interactions between the two heterocyclic rings (minimum distance 4.13 Å) due to a shift in the C(1)–Se(1)–Cu(1)–Se(1A) torsion angle (~11.08°) that results in a staggered orientation of the two five-membered rings. The copper complexes 2, 3a, and 8 have no intermolecular π–π interactions as determined from inspection of their packing diagrams.

Table 2  Experimental X-ray data (EXP) vs. theoretical DFT calculations for selected bond lengths and angles for Cu(dmit)₂I(3a), Cu(dmise)₂I(2), and Cu(dmise)₂Br(8)

<table>
<thead>
<tr>
<th></th>
<th>X = I; Y = S (EXP) (3a)</th>
<th>X = I; Y = S (DFT) (2)</th>
<th>X = I; Y = Se (EXP) (3a)</th>
<th>X = I; Y = Se (DFT) (2)</th>
<th>X = Br; Y = Se (EXP) (8)</th>
<th>X = Br; Y = Se (DFT)</th>
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</thead>
<tbody>
<tr>
<td>Cu–X</td>
<td>2.5742(6)</td>
<td>2.497</td>
<td>2.5585(10)</td>
<td>2.507</td>
<td>2.4117(10)</td>
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<tr>
<td>Cu–Y</td>
<td>2.2343(10)</td>
<td>2.301</td>
<td>2.3351(8)</td>
<td>2.394</td>
<td>2.3430(7)</td>
<td>2.408</td>
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<tr>
<td>X–Cu–Y</td>
<td>111.82(19)</td>
<td>114.3</td>
<td>111.56(2)</td>
<td>111.4</td>
<td>107.98(17)</td>
<td>113.7</td>
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<tr>
<td>Y–Cu–Y</td>
<td>136.35(4)</td>
<td>131.4</td>
<td>136.87(4)</td>
<td>137.1</td>
<td>144.03(4)</td>
<td>132.6</td>
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<tr>
<td>C–Y–Cu</td>
<td>107.59(7)</td>
<td>113.2</td>
<td>105.55(13)</td>
<td>110.0</td>
<td>103.74(12)</td>
<td>110.6</td>
</tr>
<tr>
<td>Y–C(1)</td>
<td>1.715(2)</td>
<td>1.710</td>
<td>1.864(4)</td>
<td>1.871</td>
<td>1.867(4)</td>
<td>1.867</td>
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</table>

Fig. 4 X-ray crystal structure diagrams of the trans structures: A) Cu(dmise)₂I(2), B) Cu(dmit)₂I(3a), and C) Cu(dmise)₂Br(8) showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Fig. 5 Diagram showing π–π distances between heterocyclic ligands.

Treating copper halide compounds with two equivalents of dmit or CuCl with two equivalents of dmsi also results in formation of monomeric copper thione/selone complexes. X-ray structural analysis shows that Cu(dmit)₂I(3b), Cu(dmit)₂Cl
(4), Cu(dmise)2Cl (5), and Cu(dmit)2Br (7) have planar, three-coordinate geometry around the Cu⁺ ion bound to one halide anion and two terminal thione or selenone ligands. In each case, the heterocyclic rings of the thione or selenone ligands adopt a cis conformation relative to the halide atoms geometry with angles ranging from 116.8° to 123.4° for Cu(dmit)I (3b), 118.6° to 120.7° for Cu(dmit)2Cl (4), and (Fig. 6; selected bond distances and angles in Table 3).

In these complexes, the Cu⁺ ion has a distorted trigonal geometry with angles ranging from 116.8° to 123.4° for Cu(dmit)I (3b), 118.6° to 120.7° for Cu(dmit)2Cl (4), and 118.8° to 122.3° for Cu(dmit)2Br (7). The Cu–S bond distances for complexes 3b (cis-Cu(dmit)I), 4, and 7 range from 2.23 to 2.41 Å. The Cu⁺ ion in complex 5 has a distorted trigonal geometry with angles ranging from 113.9° to 125.8°, and its Cu–Se bond distance of 2.34 Å is identical to that of Cu(dmit)2Se (2.42 Å) but shorter than those found in the tetrameric complexes (2.42 Å) and 6 (2.41 Å).

Changes in the halide ligand have little effect on Cu–S bond distances, since the Cu–S bond lengths of 2.2345(10) Å for trans-Cu(dmit)I (3a), 2.2401(11) Å for cis-Cu(dmit)I (3b), 2.2376(6) Å for Cu(dmit)2Cl (4) and 2.2298(9) Å for Cu(dmit)2Br (7) are similar. The Cu–S bond distances in 3a, 3b, 4, and 7 are comparable to previously reported trigonal planar or tetrahedral coordinated copper complexes, but shorter than other reported copper thione complexes such as CuX₃(mimzSH)₃ (X = Cl, Br, I, and mimzSH = 1-methyl-1,3-imidazoline-2-thione, 2.31–2.52 Å), Cu₃I₃(Ph₃PS)(NCCH₃)_(2) (2.34 Å), and [CuBr(n-S-µ-C₆H₅NS)(p-TolP)]₂ (2.39 and 2.42 Å). Coordination of the thione ligand to copper in complexes 3a, 3b, 4, and 7 results in almost identical S–C(1) bond distances (1.71–1.72 Å), longer than the S–C(1) bond distance in the free thione ligand (1.68 Å). Increasing van der Waals radii of the halogens coordinated to copper (1.7–1.9 Å for Cl, 1.8–2.0 Å for Br, 1.95–2.12 Å for I) results in decreased C(1)–S(1)–Cu(1) bond angles; Cu(dmit)I (4; 106.1°), Cu(dmit)Br (7; 104°), and cis-Cdmit)2I (3b; average 99.5°).

The three-coordinate copper-seleno complexes Cu(dmise)2I (2), Cu(dmise)2Cl (5), and Cu(dmise)2Br (8) have identical Cu–Se bond distances of 2.34 Å, distances shorter than previously-reported copper selenium complexes such as [Cu(o-C₆H₄(SeMe)₃)]PF₆ (2.42 Å), and [Cu(C₅H₅Se)₃][BF₄] (average 2.41 Å). The Cu–Se bond length of 2.34 Å in complexes 2, 5, and 8 is longer than that in the tetrahedrally coordinated tris(pyrazolyl)copper-selone complexes.

Table 3 Experimental crystal data vs theoretical DFT calculations for selected bond lengths (Å) and angles (deg) of Cu(dmit)I (4), Cu(dmit)2Br (7), Cu(dmit)2Cl (5), and Cu(dmise)2Cl (5).

<table>
<thead>
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<th>X = Cl; Y = S (EXP) (4)</th>
<th>X = Cl; Y = S (DFT) (4)</th>
<th>X = Br; Y = S (EXP) (7)</th>
<th>X = Br; Y = S (DFT) (7)</th>
<th>X = I; Y = S (EXP) (3b)</th>
<th>X = I; Y = S (DFT) (3b)</th>
<th>X = Cl; Y = Se (EXP) (5)</th>
<th>X = Cl; Y = Se (DFT) (5)</th>
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<tr>
<td>Cu–X</td>
<td>2.2497(9)</td>
<td>2.252</td>
<td>2.3857(8)</td>
<td>2.387</td>
<td>2.5373(9)</td>
<td>2.550</td>
<td>2.238(2)</td>
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<tr>
<td>Cu–Y</td>
<td>2.2282</td>
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<td>2.285</td>
<td>2.285</td>
<td>2.2401(11)(avg.)</td>
<td>2.291</td>
<td>2.3459(14)(avg.)</td>
<td>2.392</td>
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<tr>
<td>X–Cu–Y</td>
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<td>Y–Cu–Y</td>
<td>118.62</td>
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<td>104.00(10)</td>
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<td>99.425(12)(avg.)</td>
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<td>Y–C(1)</td>
<td>1.714(2)</td>
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<td>1.717(3)</td>
<td>1.72</td>
<td>1.712(3)(avg.)</td>
<td>1.720</td>
<td>1.862(8)</td>
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Fig. 6 Crystal structure diagrams of A) Cu(dmit)I (3b), B) Cu(dmit)2Cl (4), C) Cu(dmit)2Br (7), and D) Cu(dmise)2Cl (5) displaying 50% probability density ellipsoids. Hydrogen atoms are omitted for clarity.
Coordination of the selone ligand to copper results in complexes \([\text{Tpm}^8 \text{Cu}(\text{dmise})]^+\) \((2.29–2.31 \text{ Å})\) and \(\text{Tp}^*\text{Cu}(\text{dmise})\) \((2.33 \text{ Å})\). Coordination of the selone ligand to copper results in relatively unchanged Se–C(1) bond lengths of 1.88 Å for \(1\) and 1.89 Å for \(6\), but slightly shorter Se–C(1) bond lengths for \(2\) and \(5\) \((1.86 \text{ Å})\) and \(8\) \((1.87 \text{ Å})\), relative to that of the uncoordinated dmise ligand \((1.89 \text{ Å})\). The polarizability and size differences between chloride, bromide and iodide have the most pronounced effect on the X-ray structures of complexes \(1\), \(2\), \(3a\), \(3b\), \(4\), \(5\), \(6\), \(7\), and \(8\), but have no observable effects on Cu–Se or Cu–S bond lengths.

DFT(B3PW91) geometry optimizations predict the \textit{cis} isomer to be the lowest energy configuration for each of the 1:2 Cu:thione/selone complexes. The geometries of \(3b\), \(4\), \(5\), \(7\) and \(8\) agree with the X-ray structures of Table 3 and accurately reproduce the X-H5C short contacts \((3.160, 2.711, 2.742, 2.888 \text{ Å})\) according to the DFT calculations. This attraction may be due to X-H3/4 interactions between molecules in the crystal, which would explain why the ‘attractive’ interaction is more pronounced when X is the smaller bromide \((8)\). This suggests that for the structures of \(2\), \(3a\), and \(8\), π-π interactions may actually be preferred conformations due to the weak hydrogen-bonding interactions between units of the crystal. Such a conformation would be disfavored for X = Cl due to repulsive forces at the shorter C3/4–C3/4(A) distances required for Cl–H3/4 interactions to the smaller halogen. The lack of π-π interactions in \(8\) may be explained similarly if Br–H3/4 interactions are comparable to Se–H5 interactions such that complex \(8\) maintains the face-to-face orientation of the heterocyclic rings, but twists to increase the Se–H5 interaction.

For comparison to \(1\) and \(6\), the energies of formation of the \textit{cis} 1:2 complexes from CuX(dmhit/dmise) and an additional dmhit/dmise ligand were calculated. The energy per chalcogenone is lower for the selones than the thiones \((ΔE+ZPE = –6.0–6.3 \text{ kcal mol}^{-1}\) chalcogenone\(^{-1}\)). These values are comparable to the formation energy per chalcogenone for the hypothetical 1:1 sulfur analogues \(1(S) 6(S) (–5.8–5.5 \text{ kcal mol}^{-1}\) chalcogenone\(^{-1}\), respectively). Therefore, the 1:1 clusters are energetically preferred for selones, but the similar energies per thione suggest that experimental conditions favor the 1:2 complexes.

Powder X-ray diffraction (XRD) studies of both the tetrameric and monomeric copper complexes were carried out to determine whether more than one conformer was present in the reaction products. Experimental powder XRD patterns of the copper chloride complexes \(4\) and \(5\) fully matched their simulated patterns, suggesting that only the \textit{cis} conformer is formed and corroborating DFT calculation results (supplementary information, Fig. S11–S12). In contrast, powder XRD patterns reveal the presence of both \textit{cis} and \textit{trans} conformers of Cu(dmit), \(3a\) and \(3b\) (Fig. 7) in powder samples. Diffraction patterns for Cu complexes \(1\), \(2\), \(6\), \(7\), and \(8\) also do not fully match the simulated patterns determined from their respective single crystallographic data.

**Table 4** Reduction potentials of Cu\(^{2+/+}\) and Cu\(^{+/0}\) for the copper selone and thione complexes vs. NHE

<table>
<thead>
<tr>
<th>Complex</th>
<th>(E_p) (mV)</th>
<th>(E_{pc}) (mV)</th>
<th>(ΔE) (mV)</th>
<th>(E_{1/2}) (mV)</th>
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</thead>
<tbody>
<tr>
<td>Cu(_{2})(μ-dmise)(μ-I)I(_2) (1)</td>
<td>83, –235</td>
<td>0, –986</td>
<td>1069</td>
<td>–452</td>
</tr>
<tr>
<td>Cu(_{2})(μ-dmise)(μ-I)I(_2) (1)*</td>
<td>34, –285</td>
<td>126, –664</td>
<td>92, 379</td>
<td>80, –475</td>
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<tr>
<td>CuCl(dmise); (5)</td>
<td>–139</td>
<td>–570</td>
<td>431</td>
<td>–355</td>
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<tr>
<td>CuCl(dmit); (4)</td>
<td>52</td>
<td>–620</td>
<td>672</td>
<td>–284</td>
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<tr>
<td>CuBr(dmise); (8)</td>
<td>–151</td>
<td>–584</td>
<td>432</td>
<td>–362</td>
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<tr>
<td>CuBr(dmit); (7)</td>
<td>41</td>
<td>–524</td>
<td>565</td>
<td>–241</td>
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<tr>
<td>trans-CuCl(dmit); (3a)</td>
<td>176</td>
<td>–653</td>
<td>829</td>
<td>–239</td>
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<tr>
<td>cis-Cu(dmit); (3b)</td>
<td>298</td>
<td>–651</td>
<td>949</td>
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<td>Cu(dmise), (2)</td>
<td>–117</td>
<td>–562</td>
<td>445</td>
<td>–340</td>
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</table>

\*DPV results reported for tetrameric copper complexes \(1\) and \(6\).
(supplementary information, Fig. S3–S10†), indicating that more than one conformer may be present. Attempts to grow crystals of additional conformers using different solvent systems, seeding the crystallization solution with an analogous crystal of the desired conformer, or crystallizing at low temperatures were not successful.

Generally, structural and stoichiometric predictions of metal complexes depend on the geometrical flexibility of the metal ion coupled with the steric and electronic requirements of ligands. We found that changing the halide ligand had the most profound effect on the coordination number and geometry of the resulting copper-chalcogenene complexes. Similarly to previous reports,54–63 formation of halide bridges are generally favored for the soft iodide but not for the harder chloride ligands, whereas both bridging and terminal bonding modes were observed for the bromide ligands, since bromide lies on the borderline between soft and hard Lewis bases. Formation of the tetrameric bridging selone complexes 1 and 6 are likely favored by the presence of two highly polarizable atoms, selenium and iodine or bromine, with high propensities to bridge metal centers.

The conformations observed for the three coordinate copper complexes 2, 3a, 3b, 4, 5, 7, and 8, depend on several factors, including packing forces, halide ligand, and the number and strength of stabilizing short-contact interactions between X–H or Y–H (X = I, Br, or Cl; Y = Se or S). For the trigonal complexes 2 and 3a that have intramolecular π–π interactions between the heterocyclic rings, only very weak short contact intermolecular interactions between I–H atoms of 3.18 Å exist in 3a, whereas 2 has no short-contact intermolecular interactions. In contrast, complexes without intramolecular π–π interactions (3b, 4, 5, 7, and 8) have more significant short-contact intermolecular interactions between the halides or chalcogenenes and neighboring hydrogen atoms. These short-contact interactions likely stabilize the cis conformations (or the twisted trans conformation of 8) of these complexes relative to the trans conformations of 2 and 3a, corroborating DFT results indicating that complexes with intramolecular π–π interactions were generally less stable than structures without intramolecular π–π interactions. The lack of short contact interactions in 2 and 3a suggest that these complexes may be stabilized by the intramolecular π–π interactions between the heterocyclic rings, whereas complexes 3b, 4, 5, 7, and 8 are primarily stabilized by crystal packing forces resulting from short-contact intermolecular interactions between X–H (X = Cl, Br, I, Se, and S).

In the IR spectra of the copper thione complexes, the diagnostic ν(C=S) band appears at lower wavenumbers (1171–1173 cm⁻¹) for the trigonal complexes 3, 3b, 4, and 7 compared to 1181 cm⁻¹ for uncoordinated dmit.64 In contrast, the ν(C=Se) bands are shifted to slightly higher energies (1149–1163 cm⁻¹) for complexes 1, 2, 5, 6, and 8 compared to uncoordinated dmise (1148 cm⁻¹).65,66 Although it is not clear why this difference between S and Se coordination occurs for these complexes, the shift to lower energy for ν(C=Se) upon coordination of dmit to copper may indicate weakening of the C=S bond due to copper backbonding, whereas the shift to higher energy for ν(C=Se) upon dmise coordination to copper may indicate a slight strengthening of the C=Se bond due to Cu–Se donor bond formation. These same trends were observed for tetrahedrally coordinated copper-thione (ν(C=S) 1172–1178 cm⁻¹) and copper-selone (ν(C=Se) 1150–1151 cm⁻¹) complexes19 as well as Zn2+ and Cd2+ complexes of these ligands.12,18,67 DFT calculations assign the C==Se/S stretching band as symmetric and asymmetric modes. For 3b, 4, 5, and 7, the lower-frequency asymmetric mode is more intense, whereas the symmetric stretch is more intense for the face-to-face complexes 2, 3a, and 8.

For all the copper complexes 1–8, the 1H NMR resonances for the methyl and olefinic protons of the copper-bound dmise or dmit ligands are shifted downfield relative to unbound dmise or dmit, consistent with reports by Lobana, et al.,20,21,58 Rabinovich, et al.,68 and Kimani, et al.19 In the 13C{1H} NMR spectra, upfield shifts of the C-2 resonance of the dmise and dmit (both δ = 6) are also observed upon copper complexation. Similar upfield shifts for the C==Se or C==S carbon atoms were observed for the Cu+ complexes [Tpm3Cu(L)]+ and Tp6Cu(L) (L = dmit or dmise)19 The downfield shift of the olefinic proton resonances in the 1H NMR spectra, as well as similar downfield shifts of the C-4 and C-5 resonances in the 13C{1H} NMR spectra, are indicative of metal complexation and concomitant weakening of the C==S/Se bond.59,70 This explanation is consistent with the observed shift of the ν(C==S) band to lower energies upon dmit coordination, but not consistent with the observed shift of the ν(C==Se) band to lower energies, indicating differences between S and Se coordination in these complexes.

The trans conformer (3a) has thione 1H resonances at δ 3.63 and 7.32 and 13C{1H} resonances at δ 36.0, 120.4, and 155.1, whereas the cis conformer (3b) has thione 1H resonances at δ 3.59 and 7.27 and 13C{1H} resonances at δ 35.9, 120.2, and 155.9. When the cis and trans conformers were combined in a single NMR sample, a single set of resonances were observed in both the 1H and 13C{1H} NMR spectra, indicating that the two conformers interconvert in solution, a result that is consistent with electrochemical results.

77Se{1H} NMR resonances for the copper-selone complexes 1, 2, 5, 6, and 8 are shifted upfield (δ −13.4 to −75.0) upon copper coordination relative to the free dmise ligand (δ 21.8). This upfield shift is a result of the selenium atom binding to the electron-rich copper ion, but no correlation exists between Cu–Se bond lengths and 77Se{1H} NMR shifts.

Electrochemical studies of the copper halide complexes

Electrochemical properties of the copper(i)-halide complexes 1, 2, 3a, 3b, 4, 5, 6, 7, and 8 were examined by cyclic voltammetry (CV) to determine the difference in Cu2+/+ redox potential upon Cu-selone or -thione coordination. Cyclic voltammograms of these copper complexes exhibit two, one-electron, chemically-reversible potential waves for the Cu2+/+ and Cu0 redox potentials. A wave corresponding to the Cu2+/0 redox couple is observed at potentials more negative than −1000 mV vs. NHE. The Cu0 is then stripped off the electrode after switching the scan direction at a potential around −800 mV. Electrochemical studies of the three-coordinate copper complexes 2, 3a, 3b, 4, 5, 7, and 8 were carried out in acetonitrile solution with tetra-n-butylammonium phosphate electrolyte and a carbon working electrode. Complexes 2, 4, 5, 7, and 8 exhibit quasi-reversible oxidation and reduction waves, whereas complexes 1, 3a, 3b, and 6 exhibit irreversible electrochemical behavior for the Cu2+/+ couple. (Table 4). The selene complexes 2, 5, and 8 have lower Cu2+/+ reduction potentials ranging from −340 to
−362 mV compared to Cu^{2+/+} reduction potentials of the analogous thione complexes 3a, 3b, 4, and 7, which range from −177 to −284 mV (CV voltammograms are provided in the supplementary information, Fig. S13). Additionally, the thione-copper complexes show larger peak separations between the cathodic and anodic waves compared to the copper selone complexes. The large peak separations of the copper thione complexes may indicate instability of the oxidized products during the voltammetry sweep due to slow electron transfer kinetics.71

The copper selone complexes CuX(dmise)2 (X = I, Br and Cl) have reduction potentials more negative by an average of 108 mV relative to the copper thione complexes CuX(dmmit)2, (X = I, Br and Cl), consistent with previous reports. The CuI(dmmit) complex 3b (cis-conformation, −177 mV) has a more positive Cu^{2+/+} reduction potential than 3a (trans-conformation, −239 mV). A mixed sample of the two conformers revealed a single Cu^{2+/+} reduction potential at −256 mV (Fig. 13G; supplementary information†); these results coupled with 1H and 13C NMR data indicate that these conformers interconvert in solution.

Cyclic voltammograms for CuCl(dmmit)2, (4), CuCl(dmise)2, (5), CuBr(dmmit)2, (7), CuBr(dmise)2, (8), exhibit two, one-electron, waves belonging to Cu^{2+/+} and Cu^{+0} redox potentials. In contrast, cyclic voltammograms of CuCl(dmise)(μ-I)2, (1), Cu(dmise)2, (2), CuI(dmmit)2, (3a), CuI(dmmit)2, (3b), and CuI(dmise)(μ-Br)Br2, (6) show three distinct reduction waves. Two of the waves correspond to Cu^{2+/+} and Cu^{+0} redox potentials. The third reduction wave likely corresponds to I⁻/I₃⁻ or Br⁻/Br₂⁻ reduction couples. As previously observed for copper halide complexes, the weakly coordinated iodide ligand in complexes 1, 2, 3a, and 3b or bromide ligand in complex 6 may undergo ligand substitution with solvent acetonitrile resulting in the observed halogen reduction peaks. DPV studies of complexes 1 and 6 exhibit two distinct reduction and oxidation peaks in their voltammograms, corresponding to Cu^{2+/+} and their respective halogen redox potentials (supplementary information, Figs. S14 and S15†). Thus, the tetrameric copper complexes 1 and 6 exhibit a single Cu^{2+/+} reduction potential at −452 and −365 mV, respectively, despite having two different copper centers with different geometries.

The changes in Cu^{2+/+} reduction potentials for the three-coordinate complexes 2, 3a, 3b, 4, 5, 7, and 8 are correlated to the coordinated halide and chalcogeno ligands. For the copper thione complexes, reduction potentials are shifted to lower voltages in the following order: CuI(dmmit)2, (3b, −177 mV), CuBr(dmmit)2, (7, −241 mV), and CuCl(dmmit)2, (4, −284 mV), a trend previously observed for copper halide complexes.72 Less polarizable halide ligands stabilize Cu⁺ relative to Cu²⁺, resulting in a more negative Cu^{2+/+} reduction potential for the copper thione complexes. The analogous copper selone complexes have more negative potentials relative to the thione complexes, but the trend observed for the thione complexes is not fully followed: CuI(dmise)2, (2, −340 mV), CuCl(dmise)2, (5, −355 mV), and CuBr(dmise)2, (8, −362 mV).

Experimental section

Materials

The synthesis and manipulation of all copper complexes was performed under an inert atmosphere of argon or nitrogen using standard Schlenk techniques. Acetonitrile, methanol, dichloromethane, and ether were purified using standard procedures and freshly distilled under argon atmosphere prior to use. N,N'-dimethylimidazole thione (dmmit), N,N'-dimethylimidazole thione (dmite), and [Cu(NCCH3)4][BF4] were synthesized according to published procedures. Selenium powder (Alfa Aesar), sulfur powder (Alfa Aesar), cuprous chloride (Aldrich), cuprous iodide (Aldrich), cuprous bromide (Alfa Aesar), cuprous oxide (stabilized, Aldrich), potassium iodide (Aldrich), 1-methylimidazole (VWR), and methylidioxide (VWR) were used as received.

Instrumentation

1H, 13C{1H}, and 77Se{1H} spectra were obtained on a Bruker-AVANCE 500 MHz NMR spectrometer. 1H and 13C{1H} NMR chemical shifts are reported in δ relative to tetramethylsilane (TMS) and referenced to solvent. 77Se{1H} NMR chemical shifts were externally referenced to diphenyl diselenide (δ 461),76 and reported relative to dimethyl selenide (δ 0). Electrical experiments were performed with a BAS 100B potentiostat. A three compartment cell was used with a Ag/AgCl reference electrode, a Pt counter electrode, and a carbon working electrode. Freshly distilled acetonitrile was used as the solvent with tetra-n-butylammonium phosphat as the supporting electrolyte (0.1 M). Solutions containing 1 mM analyte were deaerated for 2 min by vigorous nitrogen purge. All E1/2 values were calculated from (Epox + Epores/2) at a scan rate of 100 mV s⁻¹. Differential pulse voltammetry (DPV) experiments were conducted using a pulse amplitude of 0.080 V and a pulse width of 0.050 s, in conjunction with a scan width of 0.045 s and a pulse period of 0.200 s. The powder X-ray diffraction (XRD) patterns were measured using an angle dispersive diffractometer (Rigaku Ultima IV) with monochromated Cu-Kα (λ = 1.540) radiation at 40 kV. Infrared spectra were obtained using nujol mulls on KBr salt plates with a Magna 550 IR spectrometer. Abbreviations used in the description of vibrational data are as follows: vs, very strong; s, strong; m, medium; w, weak; b, broad. Electrospray ionization mass spectrometry (ESI-MS) was performed using a QSTAR XL Hybrid MS/MS System from Applied Biosystems via direct injection of sample (0.05 mL min⁻¹ flow rate) into a Turbo Ion spray ionization source. Samples were run under positive mode, with ion-spray voltage of 5500 V, and TOF scan mode. Melting points were determined using a Barnstead Electrothermal 9100 apparatus in silicon-grease-sealed glass capillary tubes. UV-vis spectra were collected using a Shimadzu UV-3101 PC spectrophotometer in quartz cuvettes with a path length of 1 cm. Elemental analysis was performed by Atlantic Microlabs, Inc.

Theoretical methods

Geometry optimizations were performed with the B3PW91 exchange–correlation (xc) functionals using PQS version 3.3.77 Copper and selenium were represented by the Ermier-Christiansen relativistic effective core potential.78 The copper basis set was modified to include the Couly-Hall 4p contraction.79 The Wadt-Hay RECP basis set for sulfur and the halogens were augmented with a set of diffuse s- and p-functions.80 Nitrogen, oxygen and hydrogen centers attached to non-carbon heavy atoms were
represented by the Dunning split-valence triple-ξ plus polarization function basis set (TZVP).\textsuperscript{41} Hydrocarbon fragments were double-ξ quality with polarization functions added to carbon.\textsuperscript{42} Frequency calculations were used to confirm that the reported structures are minima on the respective potential energy surfaces.

\textbf{Cu\textsubscript{2}(µ-dmise)(μ-I)}\textsubscript{2} (1)

\textbf{Method 1.} The dmise ligand (176 mg, 1 mmol) was dissolved in acetonitrile (20 mL) and this solution was cannula transferred into a solution of [Cu(CNCH\textsubscript{3})\textsubscript{2}[BF\textsubscript{4}]] (312 mg, 1 mmol) in acetonitrile (20 mL). The reaction mixture was stirred at room temperature for 1 h until the reaction mixture was clear and colorless. Into this reaction mixture was cannula transferred KI (332 mg, 2 mmol) in methanol (15 mL) and the reaction was stirred for 5 h. The solvent was removed \textit{in vacuo}, and the product was extracted using acetonitrile. Acetonitrile was removed \textit{in vacuo}, yielding a white solid. Yield: 234 mg, 16%. Single crystals for X-ray analysis were grown from slow vapor diffusion of ether into an acetonitrile-DMF solution of the complex.

\textbf{Method 2.} The dmise ligand (176 mg, 1 mmol) was dissolved in acetonitrile (20 mL) and this solution was cannula transferred into a solution of CuI (190 mg, 1 mmol) in acetonitrile (20 mL). The reaction mixture was stirred at room temperature for 1 h, resulting in the formation of an insoluble white precipitate. KI (332 mg, 2 mmol) in methanol (15 mL) was cannula transferred into this reaction mixture to dissolve the precipitate, resulting in a clear solution followed by gradual formation of a second white precipitate. The mixture was stirred for 6 h, \textit{dried in vacuo}, and the desired product was extracted using acetonitrile (10 mL). The filtrate was \textit{dried in vacuo} to yield a white powder. Single crystals for X-ray analysis were grown from slow vapor diffusion of ether into an acetonitrile-DMF solution of the complex. Yield: 410 mg, 89%. Mp. 152 °C. Found: C, 26.88; N, 12.39; H, 3.61. \textsuperscript{5} UV-vis \textit{l}\textsubscript{max}, nm (ϵ\textsubscript{max}, M\textsuperscript{-1} cm\textsuperscript{-1}) in CH\textsubscript{3}CN: 246 (38,384). IR (cm\textsuperscript{-1}): 629 s, 673 s, 721 s, 744 s, 826 s, 1030 s, 1082 s, 1171 s, 1227 s, 1379 s, 1466 s, 1564 s, 2926 b. δ\textsubscript{H} (500 MHz; (CD\textsubscript{3})\textsubscript{2}SO; Me\textsubscript{4}Si): 3.63 (6H, s, 2CH\textsubscript{3}), 7.32 (2H, s, 2CH\textsubscript{2}). δ\textsubscript{C} (500 MHz; (CD\textsubscript{3})\textsubscript{2}SO; PhSeSePh): -42.8; \textit{m}/\textit{z} (ESI-MS): 318.98 [Cu(dmise)\textsubscript{2}]\textsuperscript{+}, 231.98 [Cu(dmise) + MeOH]\textsuperscript{+}, 190.96 [Cu(dmise)]\textsuperscript{+}.

\textbf{Cu(dmise)I} (2)

A dichloromethane solution (20 mL) of dmit (350 mg, 2 mmol) was cannula transferred into a solution of CuI (190 mg, 1 mmol) in ethanol (20 mL). The reaction mixture was stirred at room temperature for 6 h. The reaction mixture was reduced to about 5 mL \textit{in vacuo} and the desired product precipitated by addition of ether. The precipitate was filtered, \textit{dried in vacuo} to yield a white powder. Single crystals for X-ray analysis were grown from slow vapor diffusion of ether into an acetonitrile-dichloromethane solution of the complex. Yield 404 mg, 90%. Mp. 152 °C. Found: C, 26.51; N, 12.39; H, 3.55; requires Cu\textsubscript{6}H\textsubscript{3}CuN\textsubscript{3}Si\textsubscript{2}C\textsubscript{6}H\textsubscript{6} (500 MHz; (CD\textsubscript{3})\textsubscript{2}SO; Me\textsubscript{4}Si): 3.59 (6H, s, 2CH\textsubscript{3}), 7.40 (2H, s, 2CH\textsubscript{2}). δ\textsubscript{C} (500 MHz; (CD\textsubscript{3})\textsubscript{2}SO; (CD\textsubscript{3})\textsubscript{2}SePh): 35.88 (CH\textsubscript{3}), 120.22 (CH), 155.87 (C=S); \textit{m}/\textit{z} (ESI-MS): 318.98 [Cu(dmise)\textsubscript{2}]\textsuperscript{+}, 222.98 [Cu(dmise) + MeOH]\textsuperscript{+}, 190.96 [Cu(dmise)]\textsuperscript{+}.

\textbf{Cu(dmise)I,2} (3a)

\textbf{Method 1.} A dichloromethane solution (20 mL) of dmit (260 mg, 2 mmol) was cannula transferred into a solution of CuI (190 mg, 1 mmol) in acetonitrile (10 mL). The reaction mixture was stirred at room temperature for 6 h, resulting in the formation of a white precipitate. The white precipitate was filtered and \textit{dried in vacuo} to yield a white powder. Single crystals for X-ray analysis were grown by slow vapor diffusion of ether into an acetonitrile-DMF solution in the complex. Yield: 410 mg, 92%.

\textbf{Method 2.} An acetonitrile solution (20 mL) of dmit (260 mg, 2 mmol) was cannula transferred into a solution of CuI (190 mg, 1 mmol) in acetonitrile (20 mL). The reaction mixture was stirred at room temperature for 1 h, resulting in the formation of an insoluble white precipitate. To this reaction mixture was added KI (332 mg, 2 mmol) in methanol (15 mL) to dissolve the precipitate, resulting in a clear solution that was stirred for 6 h, and then dried \textit{in vacuo}. The desired product was extracted using acetonitrile (10 mL), and the filtrate was \textit{dried in vacuo} to yield a white powder. Single crystals for X-ray analysis were grown from slow vapor diffusion of ether into acetonitrile-DMF solution. Yield: 410 mg, 89%. Mp. 152 °C. Found: C, 26.51; N, 12.39; H, 3.55. \textsuperscript{5} UV-vis \textit{l}\textsubscript{max}, nm (ϵ\textsubscript{max}, M\textsuperscript{-1} cm\textsuperscript{-1}) in CH\textsubscript{3}CN: 246 (38,384). IR (cm\textsuperscript{-1}): 629 s, 673 s, 721 s, 744 s, 826 s, 1030 s, 1082 s, 1171 s, 1227 s, 1379 s, 1466 s, 1546 s, 2926 b. δ\textsubscript{H} (500 MHz; (CD\textsubscript{3})\textsubscript{2}SO; Me\textsubscript{4}Si): 3.63 (6H, s, 2CH\textsubscript{2}), 7.32 (2H, s, 2CH\textsubscript{2}). δ\textsubscript{C} (500 MHz; (CD\textsubscript{3})\textsubscript{2}SO; Me\textsubscript{4}Si): 36.02 (CH), 120.46 (CH), 155.12 (C=S); \textit{m}/\textit{z} (ESI-MS): 318.98 [Cu(dmise)\textsubscript{2}]\textsuperscript{+}, 231.98 [Cu(dmise) + MeOH]\textsuperscript{+}, 190.96 [Cu(dmise)]\textsuperscript{+}.

cis-Cu(dmise)I,2 (3b)

A dichloromethane solution (20 mL) of dmit (260 mg, 2 mmol) was cannula transferred into a solution of CuI (190 mg, 1 mmol) in ethanol (20 mL). The reaction mixture was stirred at room temperature for 6 h. The reaction mixture was reduced to about 5 mL \textit{in vacuo} and the desired product precipitated by addition of ether. The precipitate was filtered, \textit{dried in vacuo} to yield a white powder. Single crystals for X-ray analysis were grown from slow vapor diffusion of ether into an acetonitrile-dichloromethane solution of the complex. Yield 404 mg, 90%. Mp. 152 °C. Found: C, 26.51; N, 12.39; H, 3.55; requires Cu\textsubscript{6}H\textsubscript{3}CuN\textsubscript{3}Si\textsubscript{2}C\textsubscript{6}H\textsubscript{6} (500 MHz; (CD\textsubscript{3})\textsubscript{2}SO; Me\textsubscript{4}Si): 3.59 (6H, s, 2CH\textsubscript{3}), 7.27 (2H, s, 2CH\textsubscript{2}). δ\textsubscript{C} (500 MHz; (CD\textsubscript{3})\textsubscript{2}SO; Me\textsubscript{4}Si): 35.88 (CH\textsubscript{3}), 120.22 (CH), 155.87 (C=S); \textit{m}/\textit{z} (ESI-MS): 318.98 [Cu(dmise)\textsubscript{2}]\textsuperscript{+}, 222.98 [Cu(dmise) + MeOH]\textsuperscript{+}, 190.96 [Cu(dmise)]\textsuperscript{+}.
in ethanol (20 mL). The reaction mixture was stirred at room temperature for 1 h, resulting in the formation of a white precipitate. The filtrate was removed via cannula filtration and the precipitate was dried in vacuo yielding a white powder. Single crystals for X-ray analysis were grown from slow vapor diffusion of ether into an acetonitrile–DMF–methanol solution of the complex. Yield: 313 mg, 87%. Mp. 158 °C. Found: C, 15.67; H, 4.48; requires C10H14CuN2SeCl C, 17.23; N, 3.37; Se, 24.43; requires C10H15CuSeCl2 C, 18.10; Se, 27.92.

Dichloromethane (15 mL). The reaction was stirred for 6 h, and this was cannula added a solution of dmise (175 mg, 1 mmol) in dichloromethane (10 mL). The reaction was stirred for 48 h and the solvent was reduced in vacuo yielding a white powder. Single crystals for X-ray analysis were grown from slow vapor diffusion of ether into an acetonitrile–DMF solution of the complex. Yield: 317 mg, 86%. Mp. 157 °C. Found: C, 33.76; N, 15.76; H, 4.54%. UV–vis (λmax, nm (εmax, M−1 cm−1)) in CH3CN: 261 (22,595). IR (cm−1): 663 s, 730 s, 770 vs, 803 w, 867 w, 1075 s, 1173 vs, 1242 vs, 1378 vs, 1464 vs, 1565 vs, 2924 b, 3147 w.

Complex 5 was prepared using the same procedure for 4 except that dmise (350 mg, 2 mmol) was used instead of dmite. Single crystals for X-ray analysis were grown from slow vapor diffusion of ether into an acetonitrile–DMF solution of the complex. Yield: 414 mg, 92%. Mp. 170 °C. Found: C, 26.98; N, 12.52; H, 3.51; requires C10H14CuN2SeCl C, 26.71; N, 12.47; H, 3.59%. UV–vis (λmax, nm (εmax, M−1 cm−1)) in CH3CN: 273 (9,844). IR (cm−1): 653 s, 658 s, 719 vs, 743 vs, 764 vs, 868 w, 1027 vs, 1069 b, 1149 vs, 1243 vs, 1378 vs, 1465 vs, 1570 s, 1625 w, 2916 w b. δν (500 MHz; (CD3)2SO; Me4Si): 3.66 (6H, s, 2 CH3), 7.42 (s, 2 CH2).

CuBr (144 mg, 1 mmol) was dissolved in ethanol (15 mL) and to this was cannula added a solution of dmit (175 mg, 1 mmol) in dichloromethane (15 mL). The reaction was stirred for 6 h, and the solvent was reduced in vacuo to about 5 mL, and the desired product was precipitated with ether (10 mL). The white precipitate was filtered and dried in vacuo. Single crystals suitable for X-ray analysis were grown by slow diffusion of ether into an acetonitrile–DMF solution of the complex. Yield: 450 mg, 91%. Mp. 160 °C. Found: C, 24.43; N, 11.43; H, 3.17; requires C10H14CuN2SeCl C, 24.33; N, 11.35; H, 3.27%. UV–vis (λmax, nm (εmax, M−1 cm−1)) in CH3CN: 258 (15,611). IR (cm−1): 617 w, 662 s, 740 w, 749 vs, 804 w, 854 w, 1025 w, 1087 vs, 1150 vs, 1233 vs, 1379 vs, 1394 s, 1464 vs, 1565 vs, 1599 w, 2920 b, 3094 w, 3145 w. δν (500 MHz; (CD3)2SO; Me4Si): 3.67 (6H, 2 CH3), 7.42 (s, 2 CH2), 122.36 (CH3), 146.23 (C=Se). δν (500 MHz; (CD3)2SO; PhSePh): −39.3; m/z (ESI-MS): 414.85 [Cu(dmise)]+, 270.91 [Cu(dmise) + MeOH]+, 255.04 [Cu(dmise) + OH]+, 238.89 [Cu(dmise)]2−, 158.98 [Cu(C4H4N1+)].

X-ray structural data collection and processing

Single crystals of Cu,(μ-dmise)(μ-B2)Br2 (6) and CuBr (144 mg, 1 mmol) were grown by slow diffusion of ether into an acetonitrile solution of the complex. Yield: 306 mg, 24%. Mp. 212 °C. Found: C, 18.89; N, 8.81; H, 2.60; requires C10H14CuN2SeBr2 C, 18.83; N, 8.79; H, 2.53%. UV–vis (λmax, nm (εmax, M−1 cm−1)) in CH3CN: 261 (26545). IR (cm−1): 659 s, 744 s, 770 w, 1105 s, 1150 w, 1227 s, 1261 s, 1378 vs, 1464 vs, 1563 s, 2925 b. δν (500 MHz; (CD3)2SO; Me4Si): 3.65 (6H, 2 CH3), 7.41 (2 H, s, 2 CH2). δν (500 MHz; (CD3)2SO; Me4Si): 37.43 (CH3), 122.67 (CH), 144.69 (C=Se). δν (500 MHz; (CD3)2SO; Me4Si): −75.0; m/z (ESI-MS): 414.85 [Cu(dmise)]+, 270.91 [Cu(dmise) + MeOH]+, 255.04 [Cu(dmise) + OH]+, 238.89 [Cu(dmise)]2−, 158.98 [Cu(C4H4N1+)].

Cu[dmise]2Br (7)

CuBr (144 mg, 1 mmol) was dissolved in ethanol (15 mL), and to this was cannula added a solution of dmise (350 mg, 2 mmol) in dichloromethane (15 mL). The reaction was stirred for 4 h, and the solvent was reduced in vacuo to about 5 mL, and the desired product was precipitated with ether (10 mL). The white precipitate was filtered and dried in vacuo. Single crystals suitable for X-ray analysis were grown by slow diffusion of ether into an acetonitrile solution of the complex. Yield 347 mg, 86%. Mp. 152 °C. Found C, 29.83; N, 13.84; H, 3.90; requires C10H14CuN2SeBr C, 30.04; N, 14.01; H, 4.03%. UV–vis (λmax, nm (εmax, M−1 cm−1)) in CH3CN: 261 (32,442). IR (cm−1): 671 s, 722 w, 757 vs, 1073 b, 1173 s, 1244 s, 1377 vs, 1464 vs, 1570 s, 1611 w, 2584 s, 2929 b, 3080 w, 3102 w, 3146 w, 3158 s, 500 MHz; (CD3)2SO; Me4Si): 3.68 (6H, 2 CH3), 7.25 (2H, 2 CH2). δν (500 MHz; (CD3)2SO; Me4Si): 35.65 (CH3), 119.99 (CH5), 150.36 (C=Se); m/z (ESI-MS): 318.98 [Cu(dmise)]+, 222.97 [Cu(dmise) + MeOH]+, 190.95 [Cu(dmise)]2−, 128.03 [dmise]−.

Cu(dmise)2Br (8)

CuBr (144 mg, 1 mmol) was dissolved in ethanol (15 mL), and to this was cannula added a solution of dmise (350 mg, 2 mmol) in dichloromethane (15 mL). The reaction was stirred for 48 h and resulted in the formation of a white precipitate, which was filtered and dried in vacuo. Single crystals suitable for X-ray analysis were grown by slow diffusion of ether into an acetonitrile–DMF solution of the complex. Yield 450 mg, 91%. Mp. 160 °C. Found: C, 24.43; N, 11.43; H, 3.17; requires C10H14CuN2SeBr C, 24.33; N, 11.35; H, 3.27%. UV–vis (λmax, nm (εmax, M−1 cm−1)) in CH3CN: 258 (15,611). IR (cm−1): 617 w, 662 s, 740 vs, 749 vs, 804 w, 854 w, 1025 w, 1087 vs, 1150 vs, 1233 vs, 1379 vs, 1394 s, 1464 vs, 1565 vs, 1599 w, 2920 b, 3094 w, 3145 w. δν (500 MHz; (CD3)2SO; Me4Si): 3.67 (6H, 2 CH3), 7.42 (s, 2 CH2), 122.36 (CH3), 146.23 (C=Se). δν (500 MHz; (CD3)2SO; Me4Si): −75.0; m/z (ESI-MS): 414.85 [Cu(dmise)]+, 270.91 [Cu(dmise) + MeOH]+, 255.04 [Cu(dmise) + OH]+, 238.89 [Cu(dmise)]2−, 158.98 [Cu(C4H4N1+)].
Table 5  Summary of crystallographic data for complexes 1, 2, 3a, 3b, and 4

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<th>3b</th>
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<td>C_6H_12CuInSe_5</td>
<td>C_6H_12CuInSe_5</td>
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<td>Dcₐ/Å/Mg m⁻³</td>
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Indices (min) [-14, -16, -10] [-16, -13, -13] [-18, -13, -14] [-12, -11, -18] [-12, -11, -20]

Parameters 167 98 86 85 167 85
F(000) 1366 1016 864 872 728
µ/mm⁻¹ 8.650 7.676 3.577 3.540 1.902
Collected reflections 15543 6421 6879 13385 6856
Unique reflections 2263 1674 1522 3225 1522
Final R (obs. Data)¹, R₁ 0.0341 0.0232 0.0237 0.386 0.0303
wR₁ 0.0778 0.0721 0.0576 0.0916 0.0753
Final R (all data), R₁ 0.0425 0.0395 0.0244 0.0422 0.0318
wR₁ 0.0618 0.0775 0.0583 0.0943 0.0764
Goodness of fit (S) 1.107 1.132 1.203 1.139 1.123
Largest diff. Peak 1.031 1.197 0.531 1.119 0.700
Largest diff. Hole -0.937 -0.793 -0.802 -0.982 -0.397

¹ R₁ = [Σ ||Fₒ|| - |F_c|| /Σ |F_c||; wR₁ = [(Σ w(Fₒ)² - (F_c)²)²]¹/².

Table 6  Summary of crystallographic data for complexes 5, 6, 7, and 8

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<td>V (Å³)</td>
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<td>Dcₐ/Å/Mg m⁻³</td>
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Indices (min) [-18, -8, -16] [-22, 0, 0] [-12, -11, -18] [-12, -12, -18]

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µ/mm⁻¹ 6.345 9.826 4.261 8.648
2θ range (°) 2.67–25.05 2.42–26.26 2.93–26.27 2.80–26.28
Collected reflections 10854 8409 6419 6449
Unique reflections 2713 2049 1552 1560
Final R (obs. Data)¹, R₁ 0.0684 0.0379 0.0346 0.0389
wR₁ 0.1680 0.1042 0.0906 0.1042
Final R (all data), R₁ 0.0797 0.0423 0.0404 0.0437
wR₁ 0.1868 0.1079 0.0884 0.0935
Goodness of fit (S) 1.138 1.150 1.15 0.933
Largest diff. Peak 2.050 1.693 1.15 0.933
Largest diff. Hole -0.949 -1.152 -0.489 -0.927

¹ R₁ = [Σ ||Fₒ|| - |F_c|| /Σ |F_c||; wR₁ = [(Σ w(Fₒ)² - (F_c)²)²]¹/².
were removed from subsequent structure factor calculations. In the final cycle of least squares, independent anisotropic displacement factors were refined for the non-hydrogen atoms and the methyl hydrogen atoms were fixed in “idealized” positions with C–H = 0.96 Å. Their isotropic displacement parameters were set equal to 1.5 times $U_{eq}$ of the attached carbon atom. Final refinement parameters for the structures of 1, 2, 3a, 3b, 4, 5, 6, 7, and 8 are given in Tables 5 and 6; selected bond distances and angles are provided in Tables 1, 2, and 3.

**Conclusions**

Copper halides (CuI, CuBr, and CuCl) with selone and thione ligands have been synthesized and characterized, and their crystal chemistry and variable binding modes of heterocyclic selone and thione ligands. These results highlight the rich coordination chemistry and variable binding modes of heterocyclic selone and thione ligands.

**Acknowledgements**

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**References**


77 PQS version 3.3, Parallel Quantum Solutions, Fayetteville, AR.