Dinuclear copper(I) complexes with N-heterocyclic thione and selone ligands: synthesis, characterization, and electrochemical studies†

Martin M. Kimani, a David Watts, a Leigh A. Graham, b Daniel Rabinovich, b Glenn P. A. Yapc and Julia L. Brumaghima

The synthesis, characterization, and structures of a series of homooleptic and heteroleptic copper(I) complexes supported by N-heterocyclic chalcogenone ligands is reported herein. The quasi-reversible Cu(II/I) reduction potentials of these copper complexes with monodentate (dmit or dmise) and/or bidentate (BmmMeMc, BsemMeMc, BmeMeMc, BseeMeMc) chalcogenone ligands are highly dependent upon the nature and number of the donor groups and can be tuned over a 470 mV range (−369 to 102 mV). Copper–selone complexes have more negative Cu(II/I) reduction potentials relative to their thione analogs by an average of 137 mV, and increasing the number of methylene units linking the heterocyclic rings in the bidentate ligands results in more negative reduction potentials for their copper complexes. This ability to tune the copper reduction potentials over a wide range has potential applications in synthetic and industrial catalysis as well as the understanding of important biological processes such as electron transfer in blue copper proteins and respiration.

Introduction

The chemistry of monodentate and bidentate sulfur and selenium Lewis donor ligands towards soft and borderline metals has recently received much attention due to their potential applications in catalysis,1,2 the preparation of radiopharmaceuticals,3 and in supramolecular, bioinorganic, organometallic, and coordination chemistry.4,5 Thus, great strides have been made in understanding the coordination chemistry of bis-(mercaptoimidazolyl)borate (Bmm3) and bis(mercaptoimidazolyl)-methane (Bmm8) ligands, first pioneered by Parkin6,7 and Williams,8 respectively. In contrast, the reactivity of the corresponding selenium analogs, the bis(selenoimidazolyl)borates (Bse8),9,10 bis(selenoimidazolyl)methanes (Bsem8),1,11 and related derivatives,5 remains markedly underdeveloped.

We are interested in the coordination chemistry of the aforementioned bidentate neutral ligands as well as that of the closely related bis(mercaptoimidazolyl)ethanes (Bme8) and bis(selenoimidazolyl)ethanes (Bsee8) with copper(I) to understand the fundamentals of the copper–sulfur and copper–selenium interactions and their effect on Cu(I)/Cu(II) redox potentials. The high propensity for sulfur- and selenium-containing ligands to bridge metal centers also results in diverse coordination frameworks12 and these groups are also potential synthons for the formation of heterocyclic carbenes via potassium metal reduction.13 There is also increased interest in copper chalcogenolates as single-source precursors in the synthesis of semiconductor materials via metal organic chemical vapor deposition.14

Although coordination complexes of the Bmm8Mc ligand with rhenium(i),3 iron(i),15 cobalt(i),11 rhodium(i),1,16 iridium(i),17 nickel(i),11 silver(i),18–19 gold(i/iii),19 zinc(i),20 tin(i),21 lead(ii)22,23 and antimony(iii) have8 been isolated, it is rather surprising that only one report of copper(i) derivatives has been published,19 particularly given the reported affinity of copper for sulfur- and selenium-containing ligands.24

In this work, we report the synthesis and crystal structures of a series of dinuclear, three- and four-coordinate copper(i) complexes with the aim of understanding the effect of the methylene linkers and chalcogenone donor groups on the redox potentials of the Cu(i)/Cu(II) couple. These reduction potentials are highly dependent upon S/Se ligand coordination and can be tuned in a wide potential range using a variety of monodentate and bidentate thione and selone ligands. Such
redox tuning has practical applications ranging from understanding biological processes such as electron transfer in blue copper proteins and respiration,

Results and discussion

Synthesis of dinuclear copper(i) thione and selone complexes

Homoleptic dinuclear copper complexes were synthesized via the reaction of [Cu(NCMe)₄]BF₄ with the appropriate amount of N,N-dimethylimidazole thione (dmit) or N,N-dimethylimidazole selone (dmise) in acetonitrile (eqn (1)) or bis-(mercaptoimidazolyl)methane (BmmMe), bis(selenoimidazolyl)ethane (BseeMe), and bis(selenimidazolyl)ethane (BseeMe) in a mixed-solvent system of acetonitrile and dichloromethane (eqn (2)).

\[
[Cu(NCMe)₄]BF₄ + 2.5 \text{MeCN} \longrightarrow [L_2Cu(\mu-L)CuL₂]BF₄ \quad (1) \\
\text{L = dmit}(1) \quad \text{L = dmise}(2)
\]

\[
[Cu(NCMe)₄]BF₄ + 1.5 \text{MeCN/CH}_2\text{Cl}_2 \longrightarrow [LCu(\mu-L')CuL]BF₄ \quad (2) \\
\text{L = BmmMe} \quad (3) \\
\text{L = BsmeMe} \quad (4) \\
\text{L = BmeMe} \quad (5) \\
\text{L = BseeMe} \quad (6)
\]

\[
[Cu(NCMe)₄]BF₄ \quad (1) \text{MeCN} \quad [LCu(\mu-L')CuL]BF₄ \quad (2) \\
\text{L = dmit, L' = BsmeMe} \quad (7) \\
\text{L = dmise, L' = BmmMe} \quad (8) \\
\text{L = dmise, L' = BsmeMe} \quad (9)
\]

In turn, heteroleptic dinuclear complexes of copper(i) were synthesized via a convenient two-step, one-pot synthesis by treating equimolar amounts of [Cu(NCMe)₄]BF₄ and dmit or dmise in acetonitrile, followed by cannula addition of BmmMe or BsemMe in dichloromethane (eqn (3)). Similarly, treating equimolar amounts of [Cu(NCMe)₄]BF₄ and dmise in acetonitrile followed by addition of one molar equivalent of BmmMe in dichloromethane afforded a polynuclear copper(i) complex (eqn (4)).

Structural analyses of dinuclear copper complexes

The molecular structures of several complexes have been obtained using X-ray crystallography. More specifically, single crystals suitable for X-ray diffraction studies were obtained for [(dmise)₂Cu(μ-dmise)Cu(dmise)₂][BF₄]₂·CH₃CN (2), [(BmmMe)₂Cu(μ-BmmMe)Cu(BmmMe)₂][BF₄]₂ (3), [(BsemMe)₂Cu(μ-BsemMe)Cu(BsemMe)₂][BF₄]₂ (4), [(BmeMe)₂Cu(μ-BmeMe)Cu(BmeMe)₂][BF₄]₂ (5), [(dmise)₂Cu(μ-BmmMe)₂Cu(dmise)][BF₄]₂ (7), [(dmise)₂Cu(μ-BseeMe)₂Cu(dmise)][BF₄]₂ (9), and [(BmmMe)₂Cu(μ-dmise)][BF₄]₆ (10).

The X-ray crystal structure of [(dmise)₂Cu(μ-dmise)Cu(dmise)₂][BF₄]₂·CH₃CN (2) is shown in Fig. 2, and selected bond lengths (Å) and angles (°) are given in Table 1. The structural unit of [(dmise)₂Cu(μ-dmise)Cu(dmise)₂][BF₄]₂ is made up of two copper(i) centers, with the Se atom of the dimethylimidazole selone (dmise) ligands bridging the two copper atoms, forming a bent CuSeCu core. Each copper atom is further bonded to two dmise ligands and thus each copper adopts a distorted trigonal planar geometry. The average of the
four Cu-Se distances involving terminal dmise ligands (2.35 Å) is shorter than those involving the bridging dmise ligand (2.42 Å) but is slightly longer than those in the monomeric copper selone complexes (~2.30 Å) reported by Kimani et al.27 In a similar vein, these values are comparable to those observed in the three-coordinate copper selone complexes Cu(dmise)ₓX, (X = Cl, Br, I)28 and the diphosphine selene derivative [Cu3I3{Ph2P(Se)(CH2)3-P(Se)Ph2}]2.29

The molecular structures of the isostructural complexes [[BmmMe]Cu(μ-BmmMe)Cu(BmmMe)](BF4)2 (3) and [[BsemMe]Cu(μ-BsemMe)Cu(BsemMe)](BF4)2 (4) are shown in Fig. 3 and 4, with selected bond lengths and angles given in Tables 2 and 3, respectively. The dinuclear complexes feature two terminal and one bridging bis(chalcogenone) ligands, forming “butterfly” shape [Cu₂E₂] cores (E = S, Se). Each copper(I) ion adopts a distorted tetrahedral geometry, with angles ranging from 96.45 to 123.86° for 3 and from 100.50 to 123.36° for 4. The Cu–Cu distances (2.96 and 2.97 Å for 3 and 4, respectively), significantly longer than twice the covalent radius of copper(I) (2.34 Å), precludes the existence of a copper–copper bonding interaction in these complexes. As expected, the terminal Cu–S and Cu–Se bond distances in 3 and 4 (averages 2.29 and 2.42 Å, respectively) and shorter than those involving the corresponding values involving bridging ligands (averages 2.44 and 2.52 Å, respectively).

The centrosymmetric copper complex [[BmeMe]Cu(μ-BmeMe)Cu(BmeMe)](BF4)2 (5) (Fig. 5) exhibits two copper(I) 

Table 1  Selected bond lengths (Å) and angles (°) for 2

| Cu–Se | 2.3986(9) | Se(5)–Cu(1)–Se(3) | 118.37(4) |
| Cu(2)–Se(1) | 2.4382(10) | Se(5)–Cu(1)–Se(1) | 128.31(4) |
| Cu(1)–Se(3) | 2.3460(10) | Se(3)–Cu(1)–Se(1) | 113.34(3) |
| Cu(1)–Se(5) | 2.3377(9) | Se(2)–Cu(1)–Se(4) | 133.26(4) |
| Cu(2)–Se(2) | 2.3458(11) | Se(2)–Cu(1)–Se(1) | 111.91(4) |
| Cu(2)–Se(4) | 2.3592(12) | Se(4)–Cu(1)–Se(1) | 112.68(4) |
| Cu(1)–Cu(2) | 2.6326(11) |  |

Fig. 3  The crystal structure diagram of the cation in [[BmmMe]Cu(μ-BmmMe)Cu(BmmMe)](BF4)2 (3) showing 50% probability ellipsoids. Hydrogen atoms and counterions are omitted for clarity.

Fig. 4  The crystal structure diagram of the cation in [[BsemMe]Cu(μ-BsemMe)Cu(BsemMe)](BF4)2 (4) showing 50% probability ellipsoids. Hydrogen atoms, counterions, and solvent molecules are omitted for clarity.

Table 2  Selected bond distances (Å) and angles (°) for 3

| Cu(1)–S(1) | 2.6675(17) | S(1)–Cu(1)–S(2) | 96.45(4) |
| Cu(1)–S(2) | 2.3338(15) | S(1)–Cu(1)–S(3) | 113.78(6) |
| Cu(1)–S(3) | 2.2710(16) | S(1)–Cu(1)–S(4) | 105.57(5) |
| Cu(1)–S(4) | 2.3067(15) | S(1)–Cu(1)–S(5) | 118.32(5) |
| Cu(2)–S(1) | 2.3060(15) | S(1)–Cu(1)–S(6) | 103.97(6) |
| Cu(2)–S(2) | 2.4706(16) | S(3)–Cu(1)–S(4) | 116.26(5) |
| Cu(2)–S(5) | 2.2964(16) | S(1)–Cu(2)–S(2) | 103.03(5) |
| Cu(2)–S(6) | 2.3033(14) | S(1)–Cu(2)–S(5) | 107.51(5) |
| Cu(1)–Cu(2) | 2.9741(13) | S(1)–Cu(2)–S(6) | 112.87(5) |
| Cu(1)–S(1) | 2.6675(17) | S(2)–Cu(2)–S(5) | 96.51(5) |
| Cu(1)–S(2) | 2.3338(15) | S(2)–Cu(2)–S(6) | 123.86(5) |
| Cu(2)–S(6) | 2.3033(14) | S(5)–Cu(2)–S(6) | 111.07(5) |

Table 3  Selected bond distances (Å) and angles (°) for 4

| Cu(1)–Se(1) | 2.5128(12) | Se(1)–Cu(1)–Se(2) | 100.50(4) |
| Cu(1)–Se(2) | 2.5617(13) | Se(1)–Cu(1)–Se(5) | 115.76(4) |
| Cu(1)–Se(5) | 2.4221(11) | Se(1)–Cu(1)–Se(6) | 100.21(4) |
| Cu(2)–Se(1) | 2.4315(12) | Se(2)–Cu(1)–Se(2) | 110.93(4) |
| Cu(2)–Se(2) | 2.5073(12) | Se(2)–Cu(1)–Se(6) | 113.12(5) |
| Cu(2)–Se(5) | 2.4981(12) | Se(5)–Cu(1)–Se(6) | 115.10(5) |
| Cu(2)–Se(6) | 2.4091(15) | Se(1)–Cu(2)–Se(2) | 102.43(4) |
| Cu(2)–Se(4) | 2.4267(11) | Se(1)–Cu(2)–Se(3) | 122.52(4) |
| Cu(1)–Cu(2) | 2.9616(18) | Se(1)–Cu(2)–Se(4) | 95.13(4) |
| Cu(2)–Se(2) | 2.5073(12) | Se(2)–Cu(2)–Se(4) | 107.50(4) |
| Cu(2)–Se(4) | 2.4267(11) | Se(2)–Cu(2)–Se(4) | 102.71(4) |
| Cu(1)–S(1) | 2.6675(17) | Se(3)–Cu(2)–Se(4) | 123.36(4) |
centers, each arranged in a distorted trigonal planar geometry arising from the coordination of a terminal bidentate BmeMe ligand and one of the thione moieties from a bridging bis-(monodentate) BmeMe ligand. As summarized in Table 4, the sum of angles around each copper center is 354.91° and the average C–S bond distance is 2.29 Å.

The molecular structures of [(dmit)Cu(μ-BsemMe)2Cu(dmit)](BF4)2 (7) and [(dmise)Cu(μ-BsemMe)2Cu(dmise)](BF4)2 (9) are shown in Fig. 6, with selected bond length and angles for the isostructural complexes given in Table 5. The two dinuclear complexes are centrosymmetric and exhibit rhombic Cu2Se2 cores, with all the bis(selone) ligands exhibiting the unusual bridging monodentate:bidentate (μ−κ1:κ2) coordination mode. Each copper center is coordinated to a terminal dmit or dmise ligand and three selone moieties from BsemMe ligands (one terminal and two bridging), with an overall distorted tetrahedral geometry in each case. The angles surrounding the copper centers in the two complexes are very similar, ranging from 95.38 to 118.61° for 7 and from 94.97 to 118.58° for 9. The Cu⋯Cu distances (2.73 and 2.74 Å for 7 and 9, respectively) are slightly shorter than the sum of the van der Waals radii of copper, suggesting the presence of weak Cu–Cu interactions.

The average lengths of the bridging Cu–Se bonds derived from BsemMe ligands (2.52 and 2.51 Å for 7 and 9, respectively) are longer than the average terminal Cu–Se bond lengths associated with the same ligands (2.42 Å for both complexes).

The X-ray structure of [(BmmMe)Cu(μ-dmit)]n(BF4)n (10), unlike all the ones described above, reveals the formation of a coordination polymer in which an infinite chain of four-coordinate copper(i) centers are bound to two terminal sulfur atoms from a bidentate BmmMe ligand and two sulfur atoms from bridging dmit ligands (Fig. 7 and ESI, Fig. S1†). The geo-

### Table 4: Selected bond lengths (Å) and angles (°) for 5

| Bond/Angle | 5       | 7         | 9         |
|------------|---------|-----------|-----------|
| Cu(1)–S(4) | 2.2871(16) | 2.3455(16) | 2.5349(12) |
| Cu(1)–S(3) | 2.3030(16) | 2.4222(12) | 2.4950(13) |
| Cu(1)–S(2) | 2.2900(14) | 2.3013(11) | 2.4583(13) |
| S(4)–Cu(1)–S(2) | 122.49(5) | 116.36(6) | 116.36(6) |
| S(4)–Cu(1)–S(3) | 114.70(6) | 95.38(5)  | 107.35(5)  |
| S(3)–Cu(1)–S(2) | 117.72(5) | 105.96(4) | 115.95(5)  |
in complexes 6, 8, and 10 (in the range 1.694–1.704 Å), are slightly lengthened relative to those in uncoordinated dmite (1.68 Å), and 1-methyl-4-imidazoline-2-thione (1.68 Å).

**NMR spectroscopy of dinuclear copper thione and selone complexes**

The dinuclear copper complexes were characterized by $^1$H, $^{13}$C($^1$H), $^{77}$Se($^1$H), and $^{19}$F($^1$H) NMR spectroscopy. In the $^1$H NMR spectra of dmit, dmise, BmmMe, BseeMe, and BsemMe the olefinic CH protons on the heterocyclic ring are shifted downfield by δ 0.2 to 0.5 from its position in the free ligand upon copper coordination. This same downfield shift was observed by Rabinovich et al. for [Pb$_2$(BmmMe)$_5$](ClO$_4$)$_4$, and Kimani et al. for [(Tpm)$^3$Cu(L)]$^4$ complexes, and Gardiner et al. for [Ag(mibit)]$^4$ complexes, and in Table 7. Substantial shifting of the C=Se/C=Se resonances of the dmit, dmise, BmmMe, BseeMe carbon atoms are observed upon copper complexation relative to the free ligands. Coordination of the thiones and selones via the sulfur and selenium atoms results in upfield shifts of δ 5–8 ppm for both the C=S and C=Se carbons, in agreement with previous reports.$^{34,42}$

$^{77}$Se($^1$H) NMR spectroscopy studies revealed upfield shifts for the selenium resonances in the copper complexes relative to those of unbound BsemMe and BseeMe. The $^{77}$Se($^1$H) NMR signal for complex 2 could not be obtained, whereas all the complexes with BsemMe and BseeMe ligands exhibited upfield selenium resonance shifts of ~40 ppm upon coordination to copper. This upfield shift of the $^{77}$Se($^1$H) NMR resonance upon copper binding is direct evidence that the BsemMe and BseeMe ligands bind to copper in a bidentate fashion via the selenium atoms.

| Ligand or complex | C=S (dmise) | C=Se (Se) | $^{77}$Se (ppm) |
|-------------------|-------------|-----------|----------------|
| dmit              | 162.4$^i$   | 155.6$^i$ | –6             |
| BmmMe             | 163.7$^b$   | 157.0$^b$ | 16             |
| BseeMe            | 162.3$^b$   | 155.6$^b$ | 22             |
| BsemMe            | 157.3$^i$   | 147.2     | –28            |
| [Cu(dmit)$_2$](BF$_4$)$_2$ | 158.0$^b$   | 149.7$^b$ | –28            |
| [(dmit)$_2$Cu–µ-dmit$^-$](BF$_4$)$_2$ | 155.2 | 148.0$^b$ | –43            |
| [(BmmMe)$_2$Cu–µ-BmmMe$^-$](BF$_4$)$_2$ | 150.7$^b$ | 151.6$^b$ | –24            |
| [(BseeMe)$_2$Cu–µ-BseeMe$^-$](BF$_4$)$_2$ | 157.7$^i$ | 149.3$^h$ | –26            |
| [(BsemMe)$_2$Cu–µ-BsemMe$^-$](BF$_4$)$_2$ | 158.8$^b$ | 149.0$^f$ | –26            |
| [(BmmMe)$_2$Cu–µ-dmit$^-$](BF$_4$)$_2$ | 156.6$^i$ | 158.4$^b$ |                 |

$^i$ = terminal, $^b$ = bridging.
Electrochemical studies of the dinuclear copper complexes

Cyclic voltammetry studies of the chalcogenones and their dinuclear copper complexes were conducted to determine the influence of the methylene linkers on the redox potential of the chalcogenone ligands and the change in Cu(\textit{i}/i) reduction potential upon coordination of the chalcogenone ligands to copper. All the uncoordinated chalcogenone ligands exhibit chemically reversible and quasi-reversible electrochemical behavior, with the selone ligands having more negative reduction potentials relative to the analogous thione ligands (Fig. 8 and Table 8). The unbound bidentate ethylene-bridged ligands (Bme\textsubscript{Me} and Bsee\textsubscript{Me}) have larger peak separations between the oxidized and reduced products relative to the methylene-bridged ligands (Bmm\textsubscript{Me} and Bsem\textsubscript{Me}), suggesting faster electron transfer in the latter.\textsuperscript{43}

The reduction potentials of the unbound selene ligands: dmise \(-367\text{ mV} < \text{Bsee}\textsubscript{Me} (-342\text{ mV}) < \text{Bsem}\textsubscript{Me} (-333\text{ mV})\). The analogous thione ligands follow the same trend: dmit \((-169\text{ mV}) < \text{Bme}\textsubscript{Me} (-148\text{ mV}) < \text{Bmm}\textsubscript{Me} (-118\text{ mV}), versus normal hydrogen electrode (NHE; Table 8). The reduction potentials of the free bidentate chalcogenones indicate that increasing the length of the linker from methylene to ethylene results in more negative reduction potentials.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig8}
\caption{Cyclic voltammetry (CV) scan for (A) Bmm\textsubscript{Me} (dashed lines) and Bsem\textsubscript{Me} (solid lines), (B) Bme\textsubscript{Me} (dashed lines) and Bsee\textsubscript{Me} (solid lines). All data were collected with 1 mM complex in acetonitrile.}
\end{figure}

The Cu(\textit{i}/i)and Cu(\textit{0}/0) redox potentials of the complexes \textit{versus} NHE are given in Table 8. The cyclic voltamographs (CV) of the copper complexes 1, 2, 3, 4, 5, 6, 9, and 10 exhibit two, one-electron redox potential waves belonging to the Cu(\textit{i}/i)and Cu(\textit{0}/0) couples, with the exception of complexes 7 and 8 which exhibit three, one-electron redox potential waves. The Cu(\textit{0}/0) redox couple commences at potentials more than \(-1000\text{ mV}\) vs. NHE and after switching the scan direction at potentials close to 750 mV, Cu(\textit{0}) is stripped off the electrode (Fig. 9). All the dinuclear copper thione and selone complexes exhibit one-electron Cu(\textit{i}/i) oxidation and reduction waves with large \(\Delta E\) values, indicating that these redox processes are not fully reversible (ESI, Fig. S2\textit{f}).

Upon examination of the reduction potentials for the copper complexes 1, 2, 3, 4, 5, and 6, it is clear that the selene-containing complexes exhibit more negative Cu(\textit{i}/i) reduction potentials relative to the analogous thione complexes regardless of whether the thione and selone ligands are bridging. A similar trend was reported by Kimani \textit{et al.} for the electrochemistry of only monodentate [Tpm\textsuperscript{6}Cu(X)]\textsuperscript{+} complexes (X = dmise or dmit).\textsuperscript{27}

Interestingly, increasing the length of the linker in the bidentate ligands from methylene to ethylene results in lower Cu(\textit{i}/i) reduction potentials for [Cu\textsubscript{2}(Bsee\textsubscript{Me})\textsubscript{3}](BF\textsubscript{4})\textsubscript{2} (6) \((-369\text{ mV}) compared to [Cu\textsubscript{2}(Bsem\textsubscript{Me})\textsubscript{3}](BF\textsubscript{4})\textsubscript{2} (4) \((-306\text{ mV}), and the same trend is observed for the thione complex [Cu\textsubscript{2}(Bme\textsubscript{Me})\textsubscript{3}](BF\textsubscript{4})\textsubscript{2} (5) \((-203\text{ mV}) relative to [Cu\textsubscript{2}(Bmm\textsubscript{Me})\textsubscript{3}](BF\textsubscript{4})\textsubscript{2} (3) \((-180\text{ mV}). The dinuclear copper complex 9 with both Bsem\textsubscript{Me} and dmise ligands has a lower reduction potential of \(-356\text{ mV} relative to complex 10 which has both Bmm\textsubscript{Me} and dmit ligands \(-195\text{ mV}; Table 8).\textsuperscript{27,28}

The heterogeneous dinuclear complex [(dmit)\textsubscript{2}Cu\textsubscript{2-}(Bsem\textsubscript{Me})\textsubscript{3}](BF\textsubscript{4})\textsubscript{2} (7) (ESI, Fig. S2\textit{f}) exhibits two different reduction and oxidation potentials for the Cu(\textit{i}/i) couple, whereas [(dmise)\textsubscript{2}Cu\textsubscript{2}(Bmm\textsubscript{Me})\textsubscript{3}](BF\textsubscript{4})\textsubscript{2} (8) (ESI, Fig. S2\textit{f}) exhibits three oxidation and reduction waves. One reduction and oxidation wave in the dinuclear copper complex 8 likely corresponds to the reduction potential of the bidentate Bmm\textsubscript{Me} ligand (\(E_{1/2} = -51\text{ mV}\)), whereas the remaining two waves correspond to Cu(\textit{i}/i) reduction potentials, similar to those observed for complex 7. These two different Cu(i)/i reduction potentials are only observed for the dinuclear copper complexes with mixed thione and selone ligands, and effect which has not been previously reported for copper complexes (Table 8).

The unbound dmit and dmise ligands have more negative reduction potentials than the bidentate chalcogenones (Bmm\textsubscript{Me}, Bsem\textsubscript{Me}, Bme\textsubscript{Me} and Bsee\textsubscript{Me}). The reduction potentials from the bidentate chalcogenones indicate that increasing the length of the linker from methylene to ethylene results in more negative reduction potentials. All the synthesized copper–selone complexes have more negative Cu(\textit{i}/i) reduction potentials relative to the analogous copper–thione complexes. The copper–selone complexes stabilize the Cu(\textit{i}) oxidation state more effectively than the copper–thione complexes by an average of 144 mV, consistent with previously observed results.\textsuperscript{27,28}
Table 8 Redox potentials (mV) of chalcogenone ligands and Cu(II/0) and Cu(I/0) couples for dinuclear copper complexes vs. NHE all data were collected with 1 mM compound in acetonitrile with n-butylammonium phosphate as the supporting electrolyte (0.1 M) at a scan rate of 100 mV s⁻¹

| Ligand | E_{pa} | E_{pc} | ΔE | E_{1/2} | Complex |
|--------|--------|--------|----|---------|---------|
| dmit   | 424    | −565   | 712 | −210    | Cu(dmit)BBF₄ (1) |
| dmise  | 424    | −565   | 712 | −210    | Cu(dmise)BBF₄ (1) |
| BnmMe  | 289    | −500   | 620 | −180    | Cu(BnmMe)BBF₄ (2) |
| BsemMe | −53    | 538    | 350 | −306    | Cu(BsemMe)BBF₄ (3) |
| BmeMe  | 292    | −634   | 862 | −203    | Cu(BmeMe)BBF₄ (4) |
| BseeMe | 83     | −606   | 475 | −369    | Cu(BseeMe)BBF₄ (5) |
| [dmit]Cu[μ-BsemMe]₂Cu(dmise)BBF₄ (6) | 192, −6 | −44, −478 | 223, 439 | 74, −242 |
| [dmise]Cu[μ-BsemMe]₂Cu(dmise)BBF₄ (7) | 174, −32 | 31, −608 | 149, 585 | 102, −315 |
| [dmise]Cu[μ-BsemMe]₂Cu(dmise)BBF₄ (8) | −68    | −645   | 577 | −356    |
| [BnmMe₂]Cu[μ-dmit]BBF₄ (9) | 147    | −535   | 682 | −195    |
| [BnmMe₂]Cu[μ-dmit]BBF₄ (10) | 147    | −535   | 682 | −195    |

Conclusions

Dinuclear homoleptic and heteroleptic copper(i) complexes with monodentate and bidentate chalcogenone ligands have been synthesized and characterized, and the electrochemistry of the resulting species has been investigated and compared. Treating the copper(i) starting material [Cu(NCMe)₄]BF₄ with bidentate (BnmMe, BsemMe, BmeMe, BseeMe) and monodentate chalcogenone ligands (dmit and dmise) results in the formation of dinuclear copper complexes (1, 2, 3, 4, 5, and 6). The dinuclear copper complexes adopt either trigonal or tetrahedral geometries with both terminal and bridging thione or selone ligands. The heteroleptic dinuclear copper complexes ([(dmit)Cu[μ-BsemMe]₂Cu(dmise)]BBF₄ (7) and [(dmise)Cu[μ-BsemMe]₂Cu(dmise)]BBF₄ (9)) adopt distorted tetrahedral geometry where each copper is coordinated to three selenium atoms from BsemMe ligands and one sulfur atom from dmit for 7 and one selenium atom from dmise for 9. Interestingly, the mixed ligand complex 10 consists of infinite chains of tetrahedrally coordinated Cu(i) ions bound to two sulfur atoms from a BnmMe ligand and a bridging sulfur atom from a dmit ligand.

The copper selone complexes 2, 4, 6, and 9 have more negative Cu(II/0) reduction potentials relative to their sulfur analogs (1, 3, 5, and 10), and increasing the length of the methylene linker in the bidentate chalcogenone ligands results in more negative reduction potentials for their copper complexes. This study provides detailed comparative coordination chemistry of thiones and selones with copper and its effect on the Cu(II/0) reduction potentials. Simply changing the chalcogens and denticity of the thione and selone ligands results in Cu(II/0) reduction potentials of the synthesized copper chalcogenone complexes that can be tuned in a range of 471 mV, a difference...
that would have significant effects in redox-mediated reactions.

**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, and ether were purified using standard procedures and freshly distilled under argon atmosphere prior to use. N,N'-Dimethylimidazolidine-2-carboxylic acid, m-cresol, and N,N'-dimethylformamide were used as matrix for co-crystallization. The measured potentials were corrected for junction potentials. The analyte were deaerated for 2 min by vigorous nitrogen purge.

**Instrumentation**

1H, 13C{1H}, 77Se{1H} and 19F{1H} NMR spectra were obtained on Bruker-AVANCE 300 and 500 MHz NMR spectrometers. 1H and 13C{1H} NMR chemical shifts (δ) are reported in ppm relative to tetramethylsilane (TMS) and referenced to solvent. 77Se NMR spectra were externally referenced to CCl3F (δ 0 ppm). The 77Se{1H} NMR chemical shifts were obtained in CDC13 and externally referenced to diphenyl diselenide (δ 461 ppm), and reported relative to dimethyl selenide (δ 0 ppm). All 77Se NMR chemical shifts are reported in Table 7.

**Electrochemical experiments** were performed with a BAS 100B potentiostat. A three-compartment cell was used with an Ag/AgCl reference electrode, Pt counter electrode, and a glassy carbon working electrode. Freshly-distilled acetonitrile was used as a solvent. The synthesis and manipulation of all copper complexes was performed under an inert atmosphere of argon or nitrogen using standard Schlenk techniques. Acetonitrile, methanol, and ether were purified using standard procedures and freshly distilled under argon atmosphere prior to use. N,N'-Dimethylimidazolidine-2-carboxylic acid, m-cresol, and N,N'-dimethylformamide were used as matrix for co-crystallization.

**Results and discussion**

**Complex 1**

[Dmit][BF4]2 (1) Dmmt (322 mg, 2.5 mmol) was dissolved in acetonitrile (30 mL) and cannula transferred to a solution of [Cu(NCMe)4][BF4] (312 mg, 1 mmol) in acetonitrile (20 mL). The reaction was stirred at room temperature for 3 h, and the solvent volume was reduced in vacuo to about 5 mL. The product was precipitated with diethyl ether (10 mL) to afford an off-white solid that was dried in vacuo. Yield: 74% (350 mg, 0.371 mmol). Mp = 132 °C. NMR (CD3CN): 1H δ 3.63 (s, 9, H, CH3), 6.99 (s, 2, H, CH); 13C{1H} δ 35.1 (CH3), 120.4 (CH), 157.3 (C=Se). IR (cm⁻¹): 521 s, 672 vs, 746 vs, 801 s, 1047 b, 1175 vs, 1236 vs, 1284 v, 1378 s, 1464 vs, 1569 vs, 1684 w, 2276 s, 2304 s, 2723 w, 2859 b, 3118 w, 3142 w. MALDI-TOF-MS: 391.59 [Cu(dmit)2]⁺. Anal. Calc. for C65H40CuN2O2S2: C, 51.89; N, 3.80; S. Found: C, 51.87; N, 3.78; S.

**Complex 2**

[(dmise)2Cu(μ-dmise)Cu(dmise)2][BF4]2 (2) Complex 2 was prepared following the procedure for 1 except using dmise (437 mg, 2.5 mmol) was used in place of dmit. Yield: 85% (496 mg, 0.425 mmol). Mp = 126 °C. NMR (CD3CN): 1H δ 3.69 (s, 9, H, CH3), 7.16 (s, 2, H, CH); 13C{1H} δ 37.1 (CH3), 121.6 (CH), 147.2 (C=Se); 19F{1H} δ −151.62, −151.63. IR (cm⁻¹): 521 s, 624 w, 660 s, 744 s, 933 s, 1021 b, 1238 s, 1285 s, 1378 s, 1457 s, 1570 s, 1818 w, 2252 w, 2276 vs, 2304 vs, 2918 b, 3139 w, 3172 w, 3230 w. MALDI-TOF-MS: 415.07 [Cu(dmise)2]⁺. Anal. Calc. for C57H34Cu2N2O2S4: C, 51.89; N, 3.80; S. Found: C, 51.87; N, 3.78; S.

**Complex 3**

[(BmmMe)2Cu(μ-BmmMe)Cu(BmmMe)2][BF4]2 (3) Tetrahydrofuran (5 mL) was added to a 4-dram vial containing a mixture of [Cu(NCMe)4][BF4] (131 mg, 0.414 mmol) and BmmMe (150 mg, 0.624 mmol), resulting in the immediate formation of a white solid suspended in a colorless solution. After stirring the suspension for 18 h, the product was isolated by filtration and dried in vacuo for 2 h. Yield: 88% (167 mg, 0.183 mmol). Mp = 128 °C. NMR (CD3CN): 1H δ 3.43 (s, 9, H, CH3), 6.59 (s, 6, H, CH3), 7.38 (s, 6, H, imidazole H), 7.62 (s, 6, H, imidazole H); 13C{1H} δ 35.9 (q, 13C{1H} = 142, 6 C, CH3), 56.3 (t, J=158, 3 C, CH3), 118.8 (dd, J=158, J=101, J=11, 6, C, imidazole C), 121.1 (dd, J=158, J=101, J=9, 6, C, imidazole C), 153.8 (s, 6, C, C=Se); 19F{1H} δ −151.57, −151.63. UV-visible (CH3CN): 274 nm. IR (cm⁻¹): 3173 m, 3140 m, 3119 m, 3027 w, 2903 w, 2943 m, 1575 s, 1467 vs, 1401 vs, 1378 s, 1317 m, 1286 w, 1249 s, 1125 s, 1166 m, 1064 vs, 788 m, 762 s, 742 s, 724 m, 701 w, 655 w, 521 m, 470 w. Anal. Calc. for...
[(BsemMe)Cu(μ-BsemMe)Cu(BsemMe)][BF₄]₂ (4)

BsemMe (215 mg, 0.75 mmol) was dissolved in dichloromethane (20 mL) before being cannula transferred to a solution of [Cu(NCMe)₂]BF₄ (160 mg, 0.5 mmol) in acetonitrile (10 mL). The reaction mixture was stirred at room temperature for 3 h. The solvent volume in the reaction mixture was then reduced to about 5 mL and the product was precipitated with diethyl ether. The growth of single crystals for X-ray analysis was performed from slow vapor diffusion of diethyl ether into acetonitrile solution. Yield: 45% (262 mg, 0.225 mmol). Mp = 139 °C. NMR (d₆-DMSO): 1H δ 3.54 (s, 6 H, CH₃), 6.82 (s, 2 H, CH), 7.33 (d, J₉H = 2.0, 2 H, CH₂), 7.59 (d, J₉H = 2.0, 2 H, CH₂), 13C{¹H} δ 37.5 (CH₃), 59.7 (CH₃), 121.3 (CH), 123.4 (CH), 149.7 (C=Se); ¹⁹F{¹H} δ −151.59, −151.63. UV-vis (CH₃CN): 292 nm. IR (cm⁻¹): 460 s, 473 w, 521 v, 604 v, 655 s, 675 s, 731 vs, 779 w, 797 s, 1059 b, 1207 s, 1234 s, 1249 s, 1318 s, 1378 s, 1464 vs, 1575 vs, 1676 vs, 2727 b, 3145 s, 3200 w. Mass spectrum (ESI-MS): m/z 1216.59 [Cu₂(BsemMe)₃][BF₄]⁺, 882.68 [Cu₂(BsemMe)₂][BF₄]⁺, 796.67 [Cu₂(BsemMe)⁺]²⁺, 398.83 [Cu(BsemMe)⁺]⁻. Anal. Calc. for C₂₅H₁₈Cu₂N₁₂Se₆B₂F₈: C, 26.79; N, 12.49; H, 3.15. Found: C, 26.77; N, 12.49; H, 3.12%.

([dmit]Cu(μ-BsemMe)₂Cu[dmit])[BF₄]₂ (7)

Dmit (129 mg, 1 mmol) was dissolved in acetonitrile (20 mL) and cannula transferred to a solution of [Cu(NCMe)₂]BF₄ (312 mg, 1 mmol) in acetonitrile (10 mL). The reaction was stirred at room temperature for 3 h, resulting in the formation of a yellow solution. To this reaction mixture was cannula added BsemMe (336 mg, 1 mmol) in dichloromethane (10 mL) and stirred overnight. The solvent volume was reduced in vacuo to about 3 mL and the product was precipitated with diethyl ether to afford an off-white solid, which was dried in vacuo. Yield: 38% (427 mg, 0.378 mmol). Mp = 209 °C. NMR (CDCl₃): 1H δ 3.60 (s, 6 H, CH₃), 3.62 (s, 6 H, CH₃), 6.65 (s, 2 H, CH₂), 6.98 (s, 2 H, CH), 7.23 (d, J₉H = 2.5, 2 H, CH), 7.38 (d, J₉H = 2.0, 2 H, CH), 13C{¹H} δ 35.8 (CH₃), 37.8 (CH₃), 60.5 (CH₂), 120.0 (CH), 121.0 (CH), 123.3 (CH), 151.6 [C=Se(BsemMe)²⁺], 157.7 [C=Se(dmit)], 19F{¹H} δ −151.52, −151.57. UV-vis (CH₃CN): 274 nm. IR (cm⁻¹): 508 s, 521 s, 611 s, 640 s, 650 s, 657 s, 676 s, 723 vs, 746 vs, 790 vs, 839 s, 867 s, 1033 b, 1145 s, 1177 s, 1207 s, 1229 s, 1249 s, 1290 s, 1321 s, 1372 s, 1395 s, 1465 s, 1571 vs, 1602 s, 1673 s, 2920 b, 3088 w. Mass spectrum (ESI-MS): m/z 732.73 [Cu₂(BsemMe)⁺], 526.85 [dmit-Cu(BsemMe)⁺], 398.82 [Cu(BsemMe)⁺], 318.97 [Cu(dmit)⁺], 190.95 [Cu(dmit)⁻]. Anal. Calc. for C₂₃H₁₂Cu₂N₁₂Se₂B₂F₂: C, 27.44; N, 13.72; H, 3.29. Found: C, 27.28; N, 13.60; H, 3.27%.

Single crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into an acetonitrile solution of the complex.

[[dmit]Cu(μ-BmmM)₂Cu[dmit]][BF₄]₂ (8)

Complex 8 was prepared following the same procedure for 7 except that dmit (176 mg, 1 mmol) was used in place of dmit and BmmM (242 mg, 1 mmol) was used in place of BsemMe. Yield: 30% (347 mg, 0.302 mmol). Mp = 174 °C. NMR (CDCl₃): 1H δ 3.52 (s, 6 H, CH₃), 4.63 (s, 4 H, CH₂), 7.18 (d, 2 H, CH), 7.30 (d, 2 H, CH); 13C{¹H} δ 35.6 (CH₃), 45.7 (CH₂), 119.7 (CH), 120.9 (CH), 155.2 [¹⁹F{¹H} δ −148.31, −148.35. UV-vis (CH₃CN): 273 nm. IR (cm⁻¹): 501 w, 522 w, 622 w, 670 s, 680 s, 720 vs, 736 vs, 1059 vs, 1137 w, 1197 s, 1227 s, 1247 vs, 1287 w, 1378 vs, 1415 vs, 1466 v, 1570 vs, 1694 w, 2927 b, 3137 w. Anal. Calc. for C₂₉H₁₀Cu₂N₁₂Se₂B₂F₂: C, 29.88; N, 13.68; H, 3.45%.

[(BmmMe)²Cu(μ-BmmMe)²Cu(BmmMe)][BF₄]₂ (6)

Complex 6 was prepared following the procedure for 4 except that BmmMe (223 mg, 0.75 mmol) was used in place of BsemMe. Yield: 30% (174 mg, 0.153 mmol). Mp = 270 °C. NMR (d₆-DMSO): 1H δ 3.58 (s, 6 H, CH₃), 4.73 (s, 4 H, CH₂), 7.33 (d, 2 H, CH), 7.47 (d, 2 H, CH); 13C{¹H} δ 39.7 (CH₃), 47.5 (CH₂), 121.5 (CH), 122.8 (CH), 148.0 (C=Se); ¹⁹F{¹H} δ −148.10, −148.16. UV-vis (CH₃CN): 288 nm. IR (cm⁻¹): 522 s, 666 vs, 724 vs, 738 vs, 747 vs, 800 w, 930 w, 1057 vs, 1128 vs, 1183 vs, 1223 s, 1246 vs, 1287 w, 1378 vs, 1409 vs, 1467 vs, 1569 vs, 2854 vs, 2919 b, 3114 w, 3146 w, 3173 w. Anal. Calc. for C₂₉H₄₆Cu₂N₁₂Se₂B₂F₄: C, 26.79; N, 12.49; H, 3.15. Found: C, 26.97; N, 12.48; H, 3.12%.
μF_{(max)} [14, 17, 19, 22, 12, 11, 13] c

Final

\text{R} \quad \text{dmit), 6.49 (s, 2 H, C}_{\text{ss}}, 1395 \text{vs}, 1464 \text{vs}, 1572 \text{vs}, 1684 \text{b}, 2250 \text{s}, 2725 \text{s}, 2921 \text{b}, 670 \text{vs}, 729 \text{vs}, 760 \text{s}, 782 \text{s}, 848 \text{s}, 1032 \text{b}, 1174 \text{s}, 1234 \text{vs}, 1286 \text{s}, 1395 \text{vs}, 1464 \text{vs}, 1572 \text{vs}, 1684 \text{b}, 2250 \text{s}, 2725 \text{s}, 2921 \text{b}, 3140 \text{b). Anal. Calc. for C}_{28}\text{H}_{46}\text{Cu}_{2}\text{N}_{12}\text{Se}_{2}\text{F}_{6}: \text{C}, 32.41; \text{N}, 16.20; \text{H}, 3.88. Found: C, 32.55; N, 16.15; H, 3.97%. Single crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into an acetonitrile solution of the complex.}

Complex 10 was prepared following the same procedure for 7 except that Bmm\text{Me} \quad 242 \text{mg, 1 mmol) was used instead of Bsm\text{Me}. Yield: 34% (354 mg, 0.335 mmol). Mp = 159 °C. NMR (CD_{2})\text{CN}: \delta 3.52 (s, 6 H, CH_{3}, Bmm\text{Me}), 3.62 (s, 6 H, CH_{3}, dmit), 6.49 (s, 2 H, CH_{2}), 7.00 (s, 2 H, CH), 7.06 (d, J_{HH} = 2.5, 2 H, CH), 7.25 (d, J_{HH} = 2.5, 2 H, CH); ^{13}\text{C}(\text{H}) \delta 3.91 (\text{CH}_{3}), 57.5 (\text{CH}_{2}), 119.0 (\text{CH}), 120.3 (\text{CH}), 121.5 (\text{CH}), 156.6 [C=\text{S} \text{(dmit)}, 158.4 [C=\text{S} \text{Bmm\text{Me}}]; ^{19}\text{F}(\text{H}) \delta -151.30, -151.35. UV-vis (CH_{3})\text{CN}: 268 nm. IR (cm\text{superscript}{-1}): 503 s, 521 s, 603 s, 633 s, 670 vs, 729 vs, 760 s, 782 s, 848 s, 1032 b, 1174 s, 1234 vs, 1286 s, 1395 vs, 1464 vs, 1572 vs, 1684 b, 2250 s, 2725 s, 2921 b, 3140 b. Anal. Calc. for C}_{28}\text{H}_{46}\text{Cu}_{2}\text{N}_{12}\text{Se}_{2}\text{F}_{6}: \text{C}, 32.41; \text{N}, 16.20; \text{H}, 3.88. Found: C, 32.55; N, 16.15; H, 3.97%. Single crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into an acetonitrile solution of the complex.

X-ray data collection and structural determination

Single crystals grown from vapor diffusion were mounted on a glass filament with silicon grease and immediately cooled to 168 K in a cold nitrogen gas stream. Single crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into an acetonitrile solution of [Bmim\text{Me}Cu(bmim\text{Me})][BF_{4}]_{2} (2), [(Bmm\text{Me}Cu(bmim\text{Me})][BF_{4}]_{2} (3), [(Bsm\text{Me}Cu(bmim\text{Me})][BF_{4}]_{2} (4), [(Bme\text{Me}Cu(bmim\text{Me})][BF_{4}]_{2} (5), [(Bmm\text{Me}Cu(bmim\text{Me})][BF_{4}]_{2} (7), [(Bmm\text{Me}Cu(bmim\text{Me})][BF_{4}]_{2} (9), and [(Bmm\text{Me}Cu(bmim\text{Me})][BF_{4}]_{2} (10). Intensity data were collected using a Rigaku Mercury CCD detector and an AFC8S diffractometer. The space group P2_{1} \text{Ic} for 9 was determined from the observed systematic absences. No symmetry higher than triclinic was observed for 2, 4, 5, 7, and 10 and assignment of the centrosymmetric space group option, PI, provided chemically reasonable refinement results. Data reduction including the application of Lorentz and polarization (LP) effects and absorption corrections used the CrystalClear program. The structures were solved by direct methods and subsequent Fourier difference techniques, and refined anisotropically, by full-matrix least squares, on F^{2} using SHELXTL 6.12. 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.

Table 9 Summary of crystallographic data for complexes 2, 3, 4, and 5

| Chemical formula | 2          | 3          | 4          |
|------------------|------------|------------|------------|
| F.W. (g mol\textsuperscript{-1}) | 1217.22 | 1344.19 | 1437.29 |
| Space group | P1 | P1 | P1 |
| Crystal system | Triclinic | Triclinic | Triclinic |
| a, Å | 11.71(2) | 11.97(2) | 14.997(7) |
| b, Å | 14.12(3) | 14.325(3) | 15.362(7) |
| c, Å | 14.800(3) | 15.568(3) | 17.487(8) |
| α, ° | 87.32(3) | 89.58(5) | 90.90(5) |
| β, ° | 73.78(3) | 77.29(5) | 89.63(4) |
| γ, ° | 71.01(3) | 68.93(4) | 90.90(5) |
| V, Å\textsuperscript{3} | 2220.5(8) | 2418.7(8) | 4029(3) |
| Z | 2 | 2 | 4 |
| D_{cal} mg \textsuperscript{-3} | 1.821 | 1.846 | 1.685 |
| Indices (min) | –14, –17, –18 | –14, –17, 0 | –19, –20, –23 |
| (max) | 14, 17, 19 | 14, 17, 19 | 19, 19, 22 |
| Parameters | 508 | 548 | 520 |
| F(000) | 1184 | 1296 | 2072 |
| μ, mm\textsuperscript{-1} | 5.124 | 5.462 | 1.444 |
| 2θ range, ° | 3.19–26.38 | 2.94–26.34 | 1.674–28.76 |
| Collected reflections | 18943 | 9716 | 40237 |
| Unique reflections | 8943 | 9716 | 92287 |
| Final R (obs data)\textsuperscript{a}, R_{1} | 0.0461 | 0.0470 | 0.0527 |
| wR_{2} | 0.1125 | 0.1116 | 0.1267 |
| Final R (all data), R_{1} | 0.0616 | 0.0666 | 0.0682 |
| wR_{2} | 0.1263 | 0.1276 | 0.1371 |
| Goodness of fit (S) | 1.117 | 1.062 | 1.006 |
| Largest diff. peak | 1.081 | 0.817 | 1.067 |
| Largest diff. hole | 0.813 | 0.792 | 0.813 |

\textsuperscript{a} \text{R}_{1} \text{= } \left[ \frac{\sum |F_{0} \text{–}|F_{c}|]}{\sum |F_{0}|}\right. \text{R}_{2} \text{= } \left[ \sum w(|F_{0}|^{2} \text{–}(F_{c})^{2})^{2}\right]^{0.5/2}.
**Table 10** Summary of crystallographic data for complexes 7, 9, and 10

|    | 9                  | 7                  | 10                 |
|----|--------------------|--------------------|--------------------|
| F.W. (g mol⁻¹) | C₂₈H₄₀Cu₂N₁₂Se₆B₂F₈ | 1319.18            | C₂₈H₄₀Cu₂N₁₂S₆B₂F₈ | 1225.38 |
| Space group   | P1                 |                    | P2₁/c              | 1037.78 |
| Crystal system| Triclinic           |                    | Monoclinic          | 9.4763(19) |
| a, Å          | 8.21686(16)        | 11.247(2)          | 8.1987(16)         | 27.970(6) |
| b, Å          | 12.904(3)          | 12.935(3)          | 7.8016(16)         | 7.                    |
| c, Å          | 66.67(2)           | 84.64(3)           | 11.592             | 90                   |
| α°            | 84.64(3)           | 77.72(3)           | 77.75(3)           | 90                   |
| β°            | 0.76 Å             | 1.066(1)           | 1057.5(4)          | 90                   |
| γ°            | 1.16 Å             |                     | 1057.5(4)          | 2037.1(7) |
| D_24, Mg m⁻³  | 2.055              |                    | 1.924              | 2.055 |
| (max)         | [9, 14, 11]        |                    | [11, 21, 26]       | 1.924 |
| Indices (min) |                     |                    | [11, 34, 9]        | 1.692 |
| Parameters   | 266                | 636                | 2.564              | 266 |
| F(000)        | 6.194              | 3.12–26.75         | 1.359              | 1056 |
| 2θ range, °   | 2.5–26.35          | 266                | 3.09–26.31         | 1.207 |
| Collected reflections | 49066          | 2524               | 1.26–26.31         | 0.894 |
| Unique reflections | 4435              | 2421               | 0.0455             | 4906 |
| Final R (obs. data) | 0.0503            | 0.0455             | 0.1049             | 0.0440 |
| wR_2          | 0.1120             | 0.0658             | 0.0409             | 0.0984 |
| Final R (all data), R_t | 0.0796            | 0.1182             | 0.0591             | 0.0984 |
| wR_2          | 0.1319             | 1.097              | 0.1074             | 0.0591 |
| Goodness of fit (S) | 1.093              | 1.100              | 0.1046             | 0.1074 |
| Largest diff. peak | 1.158            | 1.097              | 0.1046             | 0.416 |
| Largest diff. hole | −0.736           | −0.778             | −0.424             | −0.424 |

* R_t = Σ|F_o| − |F_c| Σ|F_o|; wR_2 = (∑w(F_o^2 − (F_c)^2))/√(Σw(F_o^2)).

For complex 2, the largest peak in the final Fourier difference map (1.08 e Å⁻³) was located 0.83 Å from Se(4) and the lowest peak (−0.81 e Å⁻³) was located at a distance of 0.86 Å from Se(4). The largest peak for complex 4 in the final Fourier difference map (0.82 e Å⁻³) was located 0.08 Å from Se(4) and the lowest peak (−0.79 e Å⁻³) was located at a distance of 0.77 Å from Se(5). The largest peak for 7 in the final Fourier difference map (1.10 e Å⁻³) was located 1.23 Å from N(5) and the lowest peak (−0.78 e Å⁻³) was located at a distance of 0.88 Å from Se(1). The largest peak for 9 in the final Fourier difference map (1.16 e Å⁻³) was located 1.19 Å from H(6C) and the lowest peak (−0.74 e Å⁻³) was located at a distance of 0.92 Å from Se(1). The largest peak for 10 in the final Fourier difference map (0.42 e Å⁻³) was located 1.73 Å from S(1), and the lowest peak (−0.42 e Å⁻³) was located at a distance of 0.76 Å from Cu(1).

For complex 3, a suitable crystal was mounted using viscous oil onto a plastic mesh and cooled to the data collection temperature. Data were collected on a Bruker-AXS APEX CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The systematic absences in the diffraction data were consistent with Pnma and Pmna. The absence of a molecular mirror or inversion point, and the observed occupancy, Z = 4, were consistent with Pnma, the noncentrosymmetric option. The Flack parameter refined to zero, indicating that the true hand of the data was determined. This dataset was treated with absorption corrections based on redundant multiscan data. The structures were solved using direct methods and refined with full-matrix, least-squares procedures on F². All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. Scattering factors are contained in the SHELXTL 6.12 program library. Final refinement parameters for the structures of 2, 3, 4, 5, 7, 9, and 10 are provided in Tables 9 and 10.

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