

**Towards the synthesis of coinage metal chalcogen compounds
stabilized by a bidentate N-heterocyclic carbene**

by

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Group 11 metal chalcogen clusters have been of interest due to their potential applications in light emitting materials. Although group 11 metal chalcogen complexes with phosphine ligands have been extensively examined and most of them reported do not contain N-heterocyclic carbene (NHC) ligand. This thesis examines how the rigid bidentate NHC, 1,1'-(dibenzyl)-3,3'-(1,2-xylylene)dibenzo[*d*]imidazol-2-ylidene) (*bis*NHC^{Bn}) can be incorporated into the gold(I) metal – chalcogenolate (chalcogenolate = RSe⁻; R = organic moiety) and gold(I) chalcogenide (chalcogenide = Se²⁻) complexes. In these studies, the chalcogen reagents Se(SiMe₃)₂ or RSeSiMe₃ are reacted with the gold coordination complex [(AuOAc)₂(*bis*NHC^{Bn})] to target Au(I) selenide and Au(I) selenolate clusters with *bis*NHC^{Bn}.

The preparation, characterization, and UV-vis absorption studies of the resulting clusters are presented.

Keywords: metal chalcogenides, metal chalcogenolates, N-heterocyclic carbene ligands, luminescence.

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List of Abbreviations

Å	Angstrom
μ	Bridging
δ	Chemical shift
°C	Degrees Celsius
°C _{decomp}	Decomposition temperature
a.u.	Arbitrary units
ACN	Acetonitrile
ATR-IR	Attenuated Total Reflectance Infrared
BHT	Butylated hydroxytoluene
Bn	Benzyl
[<i>bis</i> NHC ^{Bn} H ₂] ₂ Cl ₂	1,1'-(dibenzyl)-3,3'-(1,2-xylylene)dibenzimidazolium dichloride
<i>bis</i> NHC ^{Bn}	1,1'-(dibenzyl)-3,3'-(1,2-xylylene)dibenzo[<i>d</i>]imidazol-2-ylidene
<i>bis</i> NHC ^{Me}	1,1'-(dibenzyl)-3,3'-(methylene)dibenzo[<i>d</i>]imidazol-2-ylidene
CAAC	Cyclic (alkyl)(amino) carbene
DCM	Dichloromethane
Dipp	2,6 - diisopropylphenyl
dppe	1,2 - <i>bis</i> (diphenylphosphino)ethane
dppo	1,8 - <i>bis</i> (diphenylphosphino)octane
dpppt	1,5 - <i>bis</i> (diphenylphosphino)pentane
dpepp	<i>bis</i> (2-diphenylphosphinoethyl)phenylphosphine
dbfdp	4,6-bis(diphenylphosphino)dibenzofuran

E	Chalcogen: S, Se, Te
ER	Chalcogenolate
equiv.	Equivalents
g	Grams
HOMO	Highest occupied molecular orbital
K	Kelvin
LMCT	Ligand to metal charge transfer
LUMO	Lowest unoccupied molecular orbital
MHz	Megahertz
mL	Milliliter
M	Group 11 metal
mmol	Millimole
MOAc	Metal acetate
m.p.	Melting point
MeOH	Methanol
NHC	N-heterocyclic carbene
NHC ^{Bn}	1,3-Dibenzyl-1H-benzo[d]imidazol-2-ylidene
NMR	Nuclear Magnetic Resonance
-OAc	Acetate
OLEDs	Organic Light Emitting Diodes
Ph	Phenyl
R	Organic group
RT	Room temperature

Samb V_{ca}	Salerno molecular buried volume calculation
THF	Tetrahydrofuran
% V_{bur}	Percent buried volume
UV-vis	Ultraviolet - Visible

Chapter 1

1.0 Coinage metal chalcogen compounds

1.1 Introduction

The collective name for the ore-forming elements of the periodic table is known as chalcogens, originating from the Greek words “Khalkos” and “genes”, meaning copper and born of, respectively.^{1,2} As the word implies, chalcogens are often involved in the formation of metal ores, particularly copper ores, for example cuprite, chalcocite, chalcopyrite, klockmannite, etc. These metal ores consist of three-dimensional networks and find application from paving roads to materials science and catalysis.³ Chalcogens are excellent ligands for binding multiple metal centres because of their exceptional coordination modes. Transition metal chalcogenides (TMCs) generally show a high degree of covalent bonding. In TMCs, the electronegativity difference between the metal and chalcogen is small in contrast to the more ionic alkali metal chalcogenides, as a result, the former may exhibit M-M interactions.¹

The development and design of functional materials of energy importance is one of the main goals of materials researchers. The increasing energy needs and rapid miniaturization of electronic devices in the modern world demand novel nanoscale building blocks. For instance, nanocrystals are a distinct class of nanomaterials with remarkable electrical and optical tunability. However, they intrinsically lack atomic precision due to the polydispersity and complex surface chemistry.⁴ Interestingly, a very exciting set of nanoscale building blocks attracted the scientific interest owing to their atomically precise nature, compositional and structural diversity.⁵ These molecular, atomically precise assemblies are referred to as nanoclusters (NCs).⁴ The clusters of group 11 or coinage metal chalcogens are gaining increased

attention because of their potential applications in catalysis, photovoltaic cells, luminescence signalling devices, organic light emitting diodes (OLEDs), etc.⁶⁻⁹ Additionally, the covalent nature of transition metal chalcogenides leads to unique structural properties such as modifiable band gap. The semiconducting nature along with the structural properties makes them interesting candidates to study the quantum confinement effect of late transition metal chalcogenides at the lower size limit of “quantum dots”.¹⁰⁻¹²

Coinage metal molecular clusters bridged by chalcogen atoms are a topic of importance as demonstrated in recent chemical and materials science research. The binary group 11 metal chalcogenides exhibit relatively high ionic and even higher electric conductivity in the solid state which leads to properties that are intermediate between those of semiconducting and metallic phases.¹¹ Additionally, it is of great interest to study the size-dependency of the chemical, physical, and structural properties, particularly in the transition from small molecules to bulk materials. Molecular clusters of metal chalcogenides are generally composed of a metal chalcogenide inorganic core and a stabilizing ligand shell, the latter contributes to both stability and solution processibility to the cluster core.⁴ These atomically precise, nanometer-sized metal chalcogen clusters are capable of incorporating cores composed of tens to hundreds of metal and chalcogen atoms. The complete structural information of such semiconductor nanoclusters can be obtained via single crystal X-ray diffraction.

1.2 d¹⁰- coinage metal chalcogenides, chalcogenolate nanoclusters and complexes

Chalcogens (E) are members of group 16, namely sulfur (S), selenium (Se), and tellurium (Te). Oxygen is not included here, as it exhibits low polarizability when compared to larger chalcogens such as Se and Te, primarily due to its relatively high electronegativity and smaller size.¹³ In the

case of polonium, the radioactive nature restricts its practical applications in chalcogen-related chemistry. Chalcogens are usually introduced into the metal coordination sites as either chalcogenides (E^{2-}) or chalcogenolates (RE^-) where R is an organosubstituent. The organic moiety in RE^- provides kinetic control in the assembly of desired compounds. The coordinating ability of RE^- can be modified by changing the R group and is therefore also known as “chalcogenide with a handle”.¹⁴ Both chalcogenides and chalcogenolates can adopt different bridging coordination modes (μ), which allows for the controlled synthesis of high nuclearity clusters. They can bridge two or more metal centers more efficiently than their neutral counterparts, H_2E , R_2E , and REH .¹⁵ In high-nuclearity clusters, chalcogenide ligands usually adopt two (μ_2), three (μ_3), four (μ_4) and even higher bridging modes (**Fig 1.1**). This property of multiple bridging can be exploited in forming high-nuclearity nanoclusters of coinage metal chalcogenides. The bridging modes of chalcogens with metals generally increases as one moves down the chalcogens from sulfur to tellurium. This increase in bridging coordination modes could be attributed to the increase in ionic radii and polarizability of heavier chalcogens.¹⁶

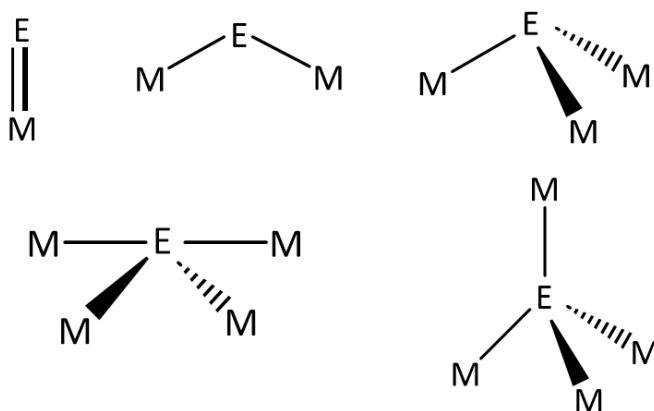
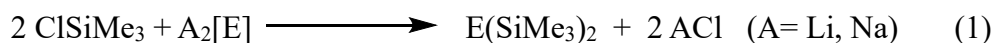


Figure 1.1: Different bridging coordination modes of chalcogenides.¹⁶

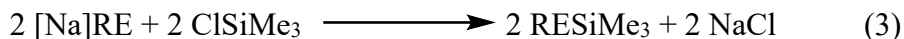
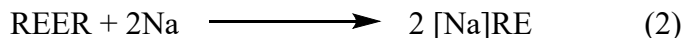
There are different ways to incorporate the chalcogen onto a metal centre. One of the earliest approaches is to introduce E^{2-} into the reaction mixture via the in-situ deprotonation of hydrogen chalcogenide, H_2E .¹⁷ Considering the toxicity of H_2S and H_2Se along with the latter leading to impure products, these reagents were generally replaced with relatively safer alkali metal chalcogenide salts to synthesize metal chalcogen clusters.¹⁷ For example, Yam et al. synthesized the first tetranuclear cluster, $[Cu_4(\mu-dppm)_4(\mu_4-S)](PF_6)_2$ (dppm= diphenylphosphinomethane) by the reaction of $[Cu_2(\mu-dppm)_2(CH_3CN)_2]^{2+}$ with Na_2S .¹⁸ In addition, they also made various Cu and Ag chalcogenide clusters by using Na_2S and Li_2Se as the chalcogen delivery agents.¹⁸ Nevertheless, the limited solubility of these chalcogenide reagents in common organic solvents prevents them from being an ideal chalcogen source.

One of the best chalcogen delivery agent developed is trimethyl silyl chalcogen reagents. The chalcogenide frameworks can be introduced via silylated chalcogen reagents such as $E(SiMe_3)_2$ and $RESiMe_3$ ($E= S, Se, Te$ and $R=$ organic moiety). They are considered better chalcogen delivery reagents owing to the solubility in common organic solvents even at low temperature allowing for a more (kinetically) controlled synthesis of desired cluster. The preparation of bis(trimethylsilyl)chalcogenides involves the addition of chlorotrimethylsilane ($ClSiMe_3$), to an alkali metal chalcogenide yielding $E(SiMe_3)_2$ as outlined in equation (1).¹⁹



The preparation of $RESiMe_3$ generally involves the reductive cleavage of diorganodichalcogenides ($REER$) in the presence of alkali metals followed by silylation with $ClSiMe_3$ as shown in equations (2) and (3), respectively.²⁰ Other typical entry points include Grignard and alkyl lithium reagents, where the elemental chalcogens are introduced into the

metal-carbon bonds of these reagents, resulting in REMgX (X = Cl, Br) and RELi, respectively, followed by silylation with ClSiMe₃.^{21,22}



E(SiMe₃)₂ and RESiMe₃ reagents are highly reactive towards coinage metal complexes (MX) (typically X= Cl, AcO) and facilitate the formation of metal chalcogen compounds with M-E or M-ER bonds in a more controlled fashion. The driving force for the reaction is the thermodynamic formation of a strong Si-X bond by the elimination of a silane (X-SiMe₃) (X= Cl, AcO) (equations (4 and 5)). The silane product has solubility in organic solvents and does not generally interfere with the crystallization of metal-containing species.²³



Silylated chalcogen reagents opened new avenues in the controlled synthesis of atomically precise high-nuclearity clusters of coinage metals. The d¹⁰- coinage metals or group 11 metals in +1 oxidation state are considered as an excellent class of metals in forming bonds with chalcogens. Coinage metal chalcogenides are formed by combining one of the metals from the group of coinage metals (Cu, Ag, and Au) together with a chalcogen element such as S, Se, and Te. Generally, the nature of the finally isolated product is influenced by the identity of the metal, chalcogen, ancillary ligand, and reaction conditions under which these components are added. This influence is best highlighted in a review by Fenske *et al.* where different copper selenide nanoclusters were synthesised as a function of reaction chemistry (**Fig 1.2**).²⁴

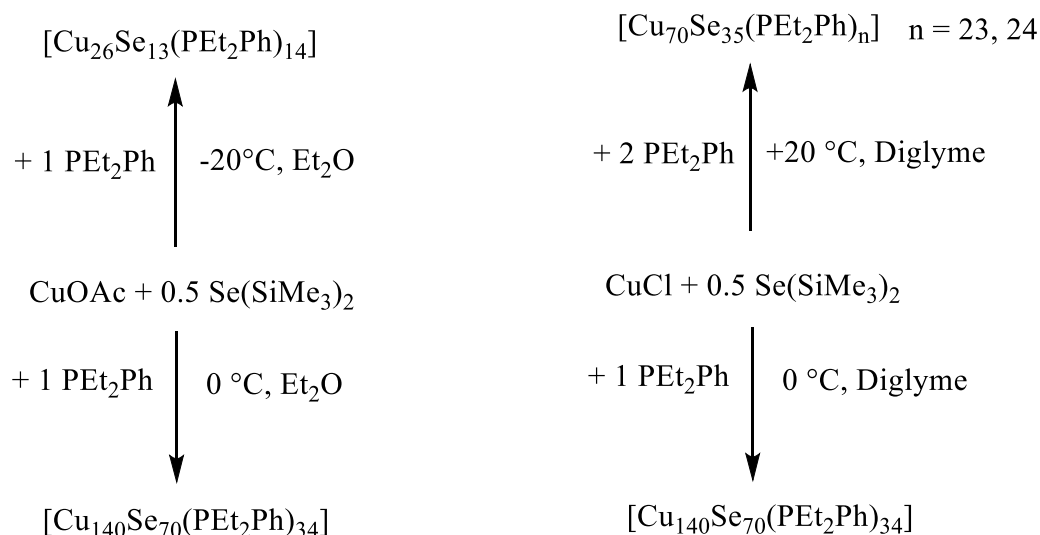


Figure 1.2: Different types of copper selenides obtained by changing the reaction chemistry. Reproduced from ²⁴.

Ancillary ligands such as phosphines (PR_3), ligands based on carbenes and organochalcogenolate anions are typically introduced onto cluster surfaces to stabilize the metal core and to reduce the number of vacant sites. These ligands prevent the nanocluster from condensing into the more thermodynamically favoured M_2E in its bulk form and act as a kinetically stabilizing, protective shell. Historically, phosphines have been used as an ancillary ligand for the synthesis of metal-chalcogen and metallic nanoclusters most widely. Nevertheless, clusters with phosphines can show poor solution stability owing to the surface dissociation of the ligand.²⁵ In this context carbene based ligands such as N-heterocyclic carbenes (NHCs) and cyclic (alkyl)(amino) carbenes (CAACs) are gaining more attention in stabilizing the d^{10} metal chalcogenide clusters. For example, the Corrigan group reported a new class of homo (one metal) and heterometallic (two or more metal types) coinage metal chalcogenide compounds stabilized by the N-heterocyclic carbene ligand, IPr = 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene).²⁶ They made five isostructural octanuclear clusters as follows; $[\text{Au}_4\text{Ag}_4(\mu_3-$

$E)_4(IPr)_4]$ ($E = S, Se$) and $[Au_8(\mu_3-E)_4(IPr)_4]$ ($E = S, Se, Te$) (**Fig 1.3**) by using gold(I) trimethylsilylchalcogenolate reagents, $[(IPr)-AuESiMe_3]$. The enhanced σ -donating ability of NHCs compared to phosphines provides exceptional stability to the resulting cluster framework.

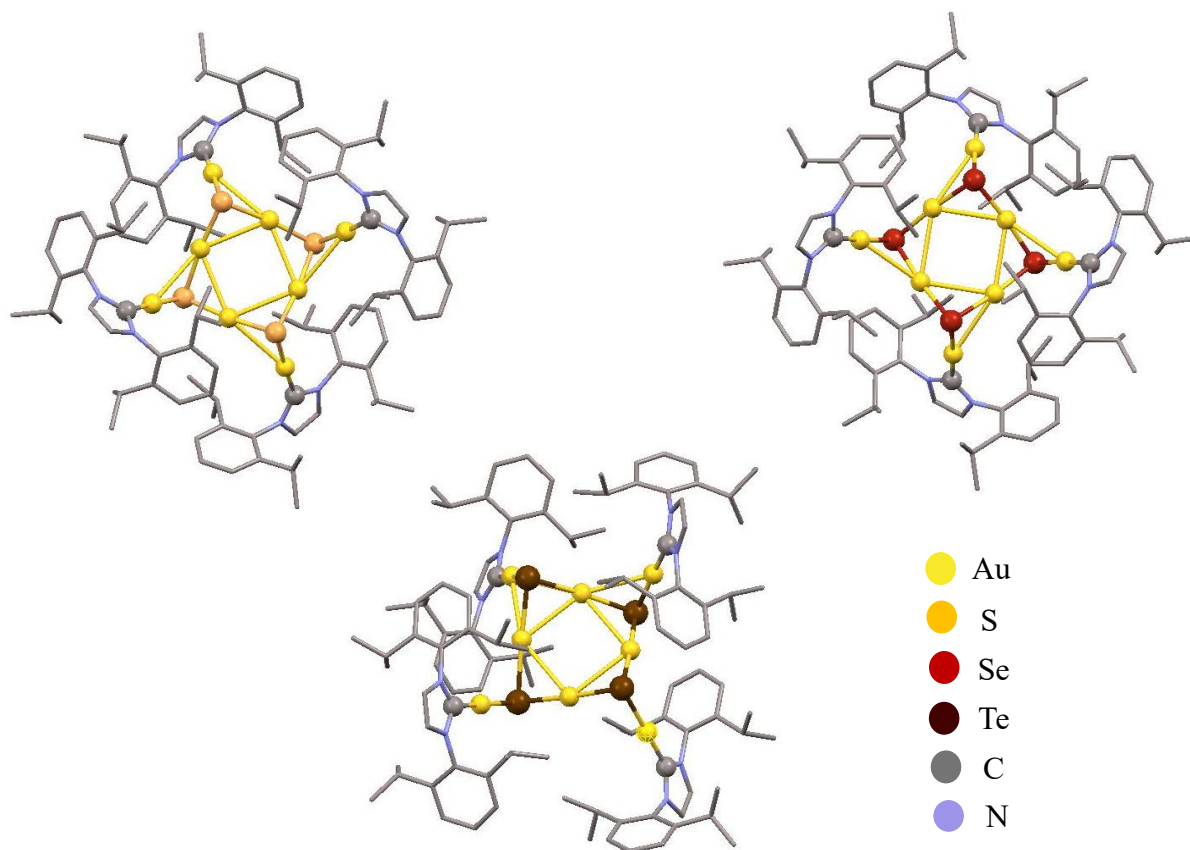


Figure 1.3: Molecular structure of $[Au_8(\mu_3-S)_4(IPr)_4]$ (top-left), $[Au_8(\mu_3-Se)_4(IPr)_4]$ (top-right) and $[Au_8(\mu_3-Te)_4(IPr)_4]$ (bottom centre) (H atoms have been omitted for clarity).²⁶

The same group reported a series of homo- and heterometallic octanuclear Cu(I)-chalcogenide clusters stabilized by cyclic (alkyl)(amino) carbenes (CAACs).²⁷ The enhanced donor properties of CAACs²⁸ compared to those of imidazole-2-ylidene-based NHCs facilitate the formation of these clusters, $[\text{Cu}_4\text{M}_4(\mu_3\text{-E})_4(\text{CAAC}^{\text{Cy}})_4]$ ($\text{M} = \text{Cu}, \text{Ag}, \text{Au}$; $\text{E} = \text{S}, \text{Se}$) where $\text{CAAC}^{\text{Cy}} = 2\text{-(2,6-diisopropylphenyl)-3,3-dimethyl-2-azaspiro[4.5]dec-1-ylidene}$ (**Fig 1.4**). These clusters were synthesised by the reaction of copper(I) trimethylsilylchalcogenolate compounds $[(\text{CAAC}^{\text{Cy}})\text{CuESiMe}_3]$ with ligand-supported group 11 metal acetates.

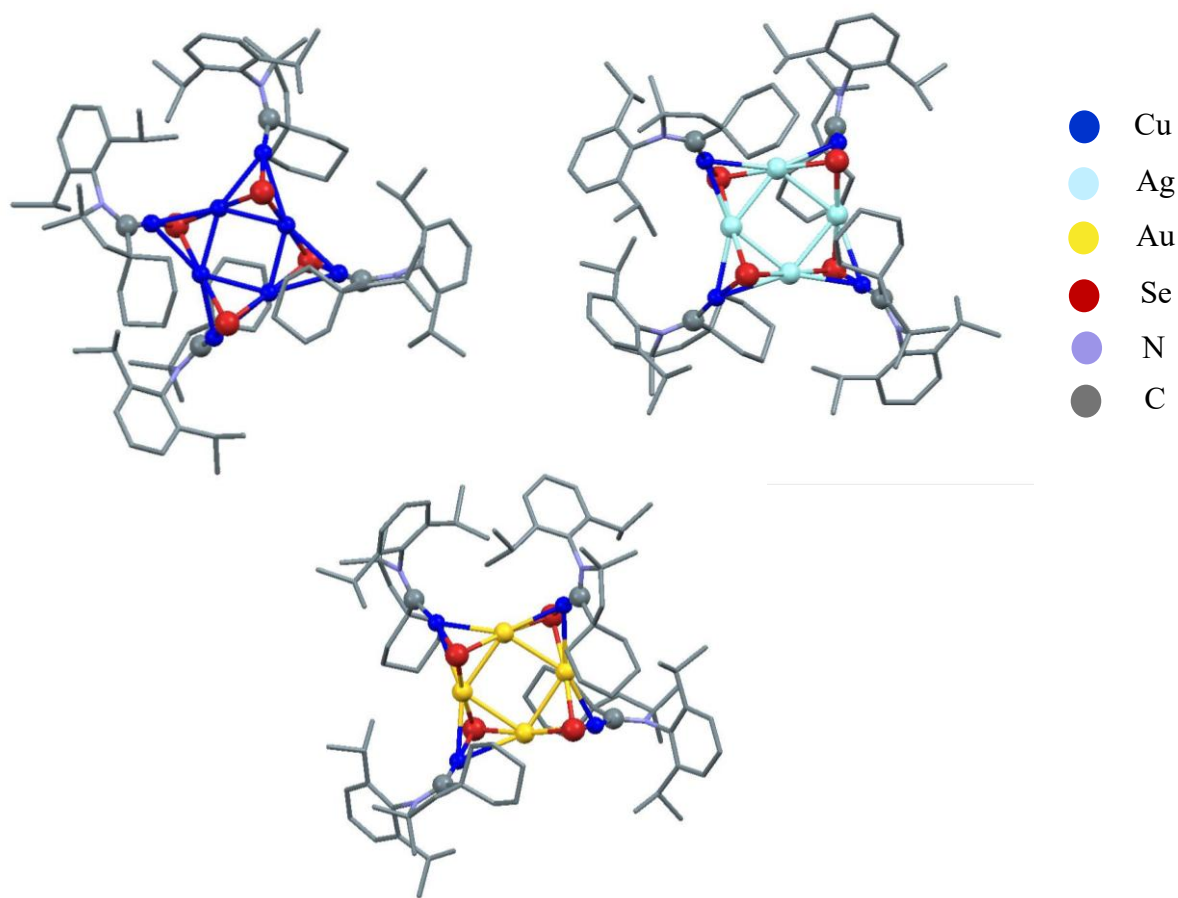


Figure 1.4: Molecular structure of $[\text{Cu}_8(\mu_3\text{-Se})_4(\text{CAAC}^{\text{Cy}})_4]$ (top-left), $[\text{Cu}_4\text{Ag}_4(\mu_3\text{-Se})_4(\text{CAAC}^{\text{Cy}})_4]$ (top-right) and $[\text{Cu}_4\text{Au}_4(\mu_3\text{-Se})_4(\text{CAAC}^{\text{Cy}})_4]$ (bottom centre) (H atoms and solvents molecules have been omitted for clarity).²⁷

1.3 N-heterocyclic carbenes as ancillary ligands on nanocluster surfaces

A carbene carbon incorporated into a heterocycle containing nitrogen is known as an N-heterocyclic carbene (NHC).²⁹ In 1991 Arduengo and co-workers reported the first representative of NHCs, 1,3-di-1-adamantylimidazol-2-ylidene.³⁰ It was a stable carbene in an oxygen and moisture free environment. The bulky adamantyl groups on the nitrogen atoms provide stability. Through crystal structure analysis, they also showed that adamantyl groups allowed for reactivity at the carbene centre while providing steric hindrance for kinetic stability. The isolation and stabilization of carbenes were a breakthrough as it was believed to be a very reactive, short-lived species for many years. This discovery attracted a lot of interest in N-heterocyclic carbenes, particularly in the field of organometallic chemistry.²⁹

These cyclic carbenes contain a two-coordinate sp^2 hybridised carbon atom with a lone pair, stabilized by neighbouring π -donating N-atoms. NHCs function similarly to σ -donor ligands with a pair of accessible electrons because of the σ orbital on the carbenic carbon (**Fig. 1.5**). Therefore, these carbon-based organic molecules can take the place of traditional monodentate ligands like amines and phosphines. Additionally, the NHCs form strong bonds with transition metals.^{31,32} Thus, they are considered as a successful class of highly nucleophilic ancillary ligands in the field of organometallic and coordination chemistry. The electronic effects resulting from the nitrogen atoms, together with the bulkiness of the N-substituents on the ring, hinder dimerization and account for the stability of the system.³³ The mesomeric interaction between lone pair on each nitrogen and vacant p-orbital of the carbene centre contributes to the overall electronic stabilization with a stabilization energy of 70 kcal.mol⁻¹. Furthermore, an additional stabilization of 25 kcal.mol⁻¹ comes from the cyclic nature influencing the electronic arrangement of the carbenic carbon.^{34,35} Therefore, NHCs can act as electron-rich nucleophilic species. The above-mentioned

structural properties lower the energy of the singlet ground state and this means that the HOMO of the NHC is the lone pair (singlet state) and the LUMO is the empty p orbital on the carbenic carbon atoms. This is in contrast to traditional carbenes, which are electrophilic because of their triplet character. Furthermore, NHCs are excellent candidates for stabilizing a variety of reactive species as they are endowed with greater σ -donating ability and relatively weaker π -accepting abilities in comparison with phosphines. Despite the fact that NHCs are weaker π -acceptors than phosphines, there is a non-negligible component of π -back-bonding in metal-NHC bonds, which in turn depends on the electron richness of the coordinating metal and energy of the LUMO.^{33,36,37} NHCs are an ideal choice of ligand for modifying and fine-tuning the reactivity and photophysical properties of the atomically precise coinage metal chalcogenide clusters. Coinage metal-NHCs have been extensively studied for their fascinating structural features and multitude of applications in the field of catalysis³⁸, medicine³⁹, surface chemistry⁴⁰ and nanocluster chemistry.⁴¹

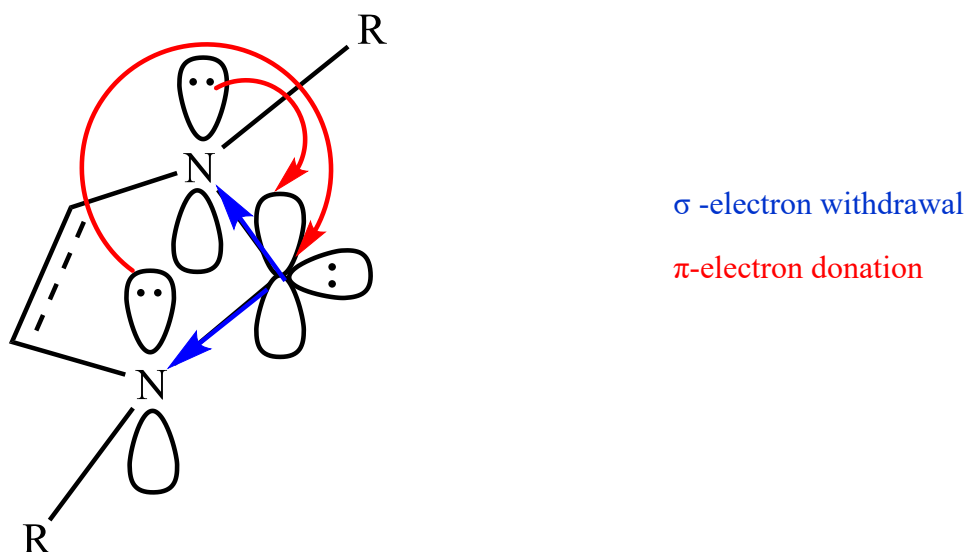


Figure 1.5: Electronic structure of NHC. Reproduced from ⁴².

1.4 Percent buried volume ($\%V_{bur}$)

A great deal of research has been done to develop a reliable steric parameter that quantifies the size of a ligand around a metal center. Tolman introduced a steric descriptor based on cone angle (θ) where the metal is placed at the vertex of a cone.⁴³ This method is still considered as the best for the calculating the size of tertiary phosphine ligands. Nevertheless, given the complexity of finding size, it was not applicable to all organometallic ligands. Interestingly, Nolan and Cavallo proposed an excellent steric descriptor called percent buried volume ($\%V_{bur}$) to define the steric bulk of all ligands.⁴⁴ $\%V_{bur}$ is defined as the percentage of the total volume occupied by any given ligand in a sphere of fixed radius as depicted in **Fig.1.6**. The metal is placed at the centre of the sphere and all the parameters used for the calculation are obtained from crystallographic data. Cavallo and co-workers developed a user-friendly online tool known as SambVca (**Salerno molecular buried volume calculation**) to calculate percent values.⁴⁵ Given that the steric characteristics of coinage metal-chalcogenide clusters are equally as significant as electronic characteristics, the calculation of $\%V_{bur}$ enables the appropriate selection of ancillary ligands based on size.^{46,47}

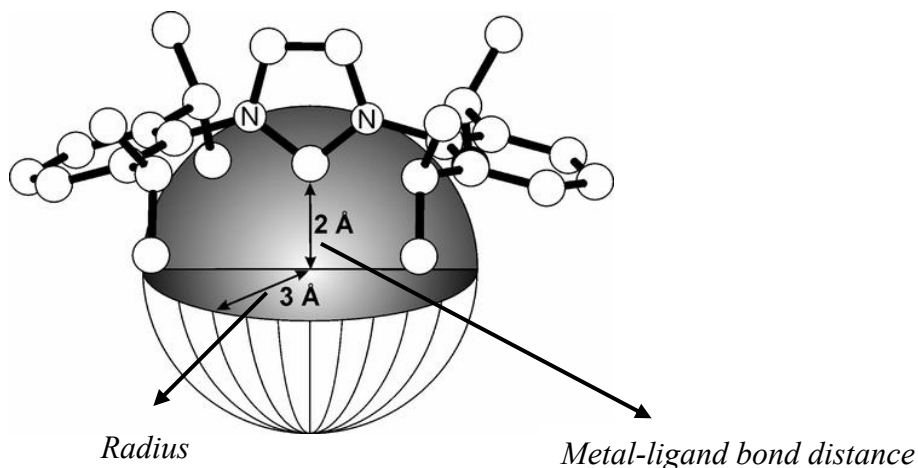


Figure 1.6: Illustration of sphere in the calculation of percent buried volume. Reproduced from ⁴⁵.

The steric impact of some selected NHCs on corresponding $[\text{AuCl}(\text{NHC})]$ species is given in **Fig 1.7**. In the case of NHC-(I), changing the backbone with an Me group results in a considerable increase in $\%V_{\text{bur}}$. When comparing NHC-(II) and NHC-(III), the effect of N-substituent is highlighted by a large increase in $\%V_{\text{bur}}$ when replacing isopropyl group with 2,6-diisopropyl phenyl (Dipp) group (28.5 vs 47.0).⁴⁸ The Au-NHC distance has been fixed at 2 Å for all the NHCs given below.

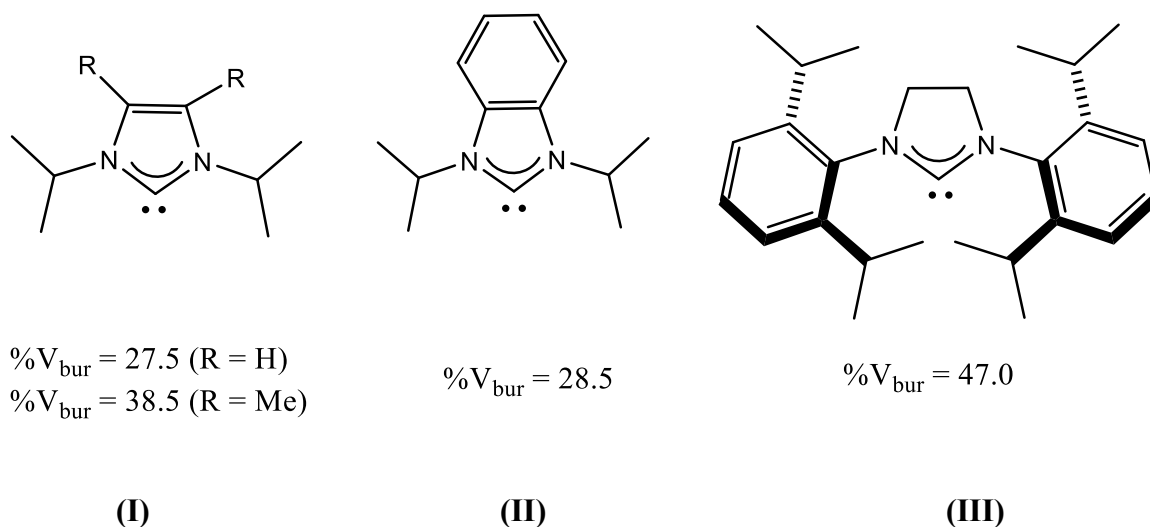


Figure 1.7: $\%V_{\text{bur}}$ of selected NHCs in $[\text{AuCl}(\text{NHC})]$.⁴⁸

1.5 Metallophilic interactions in coinage metals

Coinage metals in the +1 oxidation state often display M-M bonding and this weak attractive force between metal atoms are referred to as metallophilic interactions.⁴⁹ These weak or secondary bonds can be observed in univalent coinage metals, Au(I), Ag(I), and Cu(I). Despite being weak, these closed shell d^{10} - d^{10} interactions are found to be influencing the structural and physical features of the coinage metal compounds.⁴⁹ Metallophilic interactions in d^{10} metals continue to attract both theoretical and experimental interest, considering intriguing photophysical properties of polymetallic assemblies containing these metals, especially in Au(I) compounds.⁵⁰ Interestingly,

the metal-metal interactions in polynuclear complexes reduce the vibrations inside the cluster which in turn reduces the loss of energy in the form of vibrational energy. Auophilic (Au(I)...Au(I)) interactions are the most studied and prominent interactions among all closed shell d^{10} - d^{10} interactions. The presence of auophilicity is usually indicated by the short intermetallic distance (2.5-3.5 Å) between the gold centres.⁴⁹ The strength of Au(I)...Au(I) interactions (7-11 kcal/mol) is comparable to that in hydrogen bonding; however, they are slightly stronger than van der Waals forces. The relativistic contraction of the valence electrons is considered as the most accepted theory for the origin of auophilic interactions.⁴⁹ Au(I) complexes with N-heterocyclic carbene ligands are known to be intensely luminescent, and their emission properties may be notably influenced by intra- or inter Au(I)...Au(I) interactions.⁵¹ The emissive properties of these complexes make them suitable candidates in the field of organic light emitting diodes (OLEDs) ⁵². Furthermore, they also belong to a very promising class of brightly phosphorescent emitters because of the strong spin-orbit coupling facilitated by the heavy atom effect.⁵³ $[\text{Au}_2(\text{bisNHC}^{\text{Me}})_2]\text{Br}_2$ ($\text{bisNHC}^{\text{Me}} = 1,1'$ -(dibenzyl)-3,3'-(methylene)dibenzo[*d*]imidazol-2-ylidene) is an example of a dinuclear Au(I) complex based on methylene bridged, N-benzylbenzimidazol-2-ylidene which has a moderate auophilic interaction (**Fig 1.8**). As a result, the two Au centers bow towards one another distorting the linearity of $\text{C}_{\text{carbene}}-\text{Au}-\text{C}_{\text{carbene}}$ axes.⁵⁴

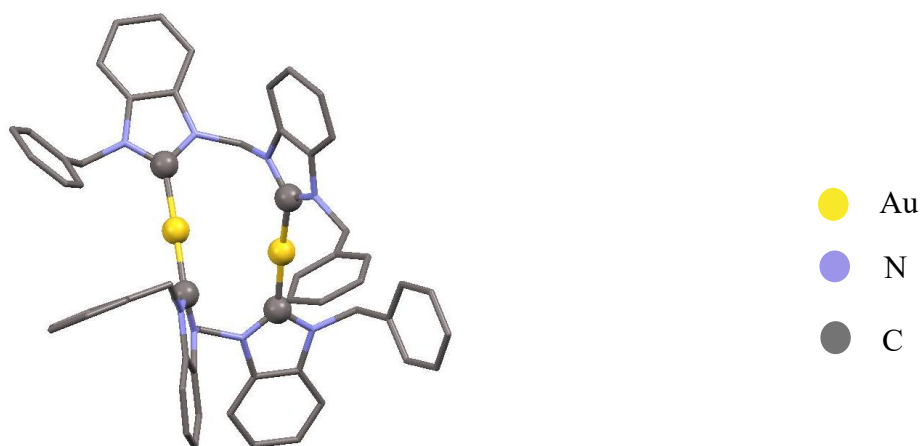


Figure 1.8: Molecular structure of $[\text{Au}_2(\text{bisNHC}^{\text{Me}})_2]\text{Br}_2$. (H atoms, anions, and solvents molecules have been omitted for clarity).⁵⁴

Similar to aurophilic contacts, argentophilic interactions are indicated by the short Ag-Ag distances ($< 2.5 - 3.4 \text{ \AA}$) in Ag(I) compounds.⁴⁹ Nevertheless, Ag(I)...Ag(I) interactions are less explored when compared to aurophilicity, mainly due to the preferred two-coordinate linear geometry in Au(I) complexes. This tendency of forming linear two-fold coordination is not that evident in Ag(I) molecular systems.

The closed shell d^{10} - d^{10} interactions in Cu(I) complexes (Cu(I)...Cu(I)) are referred to as cuprophilicity. This metallophilic interaction is considerably weaker than aurophilic and argentophilic attractive forces as the strength of cuprophilic contact is equivalent to van der Waals forces.⁴⁹ The existence of Cu(I)...Cu(I) bonding is a topic that is still under debate given the relativistic effects are more pronounced in heavier elements such as Au and Ag. The conductivity and photophysical properties of Cu(I) compounds, however, were found to be significantly influenced by cuprophilic interactions. Analogous to aurophilic and argentophilic contacts, the significant evidence for Cu(I)...Cu(I) interaction is the Cu-Cu distance. These attractive forces are

typically characterized by copper-copper distances (2.4-2.8 Å) that are shorter than the sum of the van der Waals radii (3.92 Å).⁴⁹ Therefore, cuprophilic forces are relatively weak and difficult to confirm when there exist other strong forces like hydrogen bonding, crystal packing effects, π - π interactions, etc. Single crystal X-ray diffraction provides precise information on the interaction between copper centres and is hence considered as the best analytical tool to confirm cuprophilic interactions.⁵⁵

1.6 Cu(I) and Au(I) chalcogen compounds with protective ligands on nanocluster surface

Molecular nanoclusters of Cu(I) and Au(I) combined with bridging chalcogenides (E^{2-} ; E = S, Se, Te) or chalcogenolates (RE^- ; R = organic group) ligands with protecting groups on the surface is an important area in materials science. This is primarily due to the relatively high electric and ionic conductivity of clusters of coinage metal chalcogenides in solid state.¹¹ Group 11 metals in combination with chalcogenolate forms an $(ME)_x$ core composed of M(I) and RE^{-1} . The organic ligands and R group on the periphery are bonded to the metal and chalcogen, respectively. The ability of organic substituents to alter the molecular, electronic and conductive properties makes coinage metal chalcogenolate an interesting class of modifiable complexes.^{56,57} Chalcogenolates can exhibit multiple coordination modes, leading to different structural and photophysical properties. An example of a sulfur bridged binuclear Cu(I) complex is $[Cu_2(\mu_2-S-C_6H_4-OMe)_2(dpppt)_2]$ (dpppt = diphenylphosphinopentane), where R = *p*-C₆H₄OMe.⁵⁶ This complex is composed of a copper-thiolate core with organic ligands present at the periphery. As displayed in **Fig 1.9**, the chalcogenolate adopts a μ_2 coordination. Another example of Cu(I) thiolate cluster is $[Cu_7(p-S-C_6H_4-NMe_2)_7(PPh_3)_4]$.⁵⁸ The organic ligand shell in this case is a phenyl group with a donor substituent, NMe₂. The size and structural geometry of above-mentioned Cu(I) thiolate clusters with different organic substituents are very different from each other. In $[Cu_2(\mu_2-S-C_6H_4-$

OMe)₂(dpppt)₂], each Cu atom is bonded to two thiolates and two phosphines, forming a tetrahedral geometry. However, in [Cu₇(*p*-S-C₆H₄-NMe₂)₇(PPh₃)₄], four of the seven Cu centres have a tetrahedral geometry (three bonds to thiolate and one to phosphine) while the other three Cu atoms are solely bonded to thiolates forming a trigonal planar geometry. Furthermore, the short distance between Cu centres in [Cu₇(*p*-S-C₆H₄-NMe₂)₇(PPh₃)₄] indicated cuprophilic interactions.⁵⁸

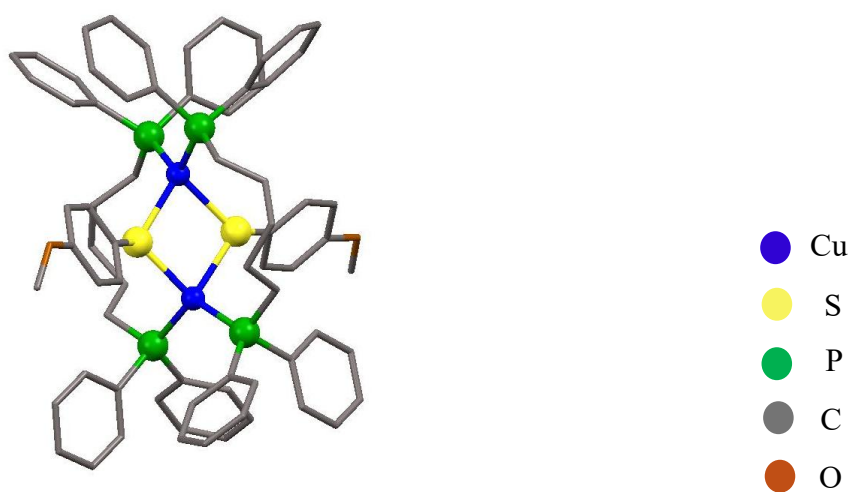


Figure 1.9: Molecular structure of [Cu₂(μ₂-S-C₆H₄-OMe)₂(dpppt)₂] (H atoms have been omitted for clarity).⁵⁶

Group 11 metal chalcogenides generally exhibit a 2:1 ratio of metal to chalcogen forming an (M₂E)_x core composed of M(I) and E²⁻ with protective ligands (usually phosphines and NHCs) bonded to (some of) the metals present on the nanocluster surface. One of the most common ligands used to stabilize metal chalcogen clusters are monodentate or bidentate phosphines.²⁴ Compounds of Cu(I) chalcogenides are receiving more scientific attention because of their diverse structural chemistry along with interesting physical and chemical properties. A large number of Cu(I) chalcogenide clusters with a Cu₂E (E = S, Se, Te) core stabilized by phosphines are

known.^{11,24} The bright-red phosphorescence emission in the solid state at room temperature is a property of complexes with a Cu_{12}E_6 ($\text{E} = \text{S}, \text{Se}$) core structure.⁵⁹ An example of such red luminescent polynuclear cluster with a ‘ Cu_{12}S_6 ’ core is $[\text{Cu}_{12}\text{S}_6(\text{dpppt})_4]$ ($\text{dpppt} = \text{bis}(\text{diphenylphosphino})\text{pentane}$) (**Fig.1.10**).⁶⁰ The cluster core is composed of Cu(I) and S^{2-} with a ratio of 2:1 with phosphine ligands on the surface bonded to the Cu atoms. In this example, S^{2-} adopts μ_4 coordination modes. The short distances between adjacent Cu atoms in this Cu_{12} cluster indicate cuprophilic contacts.⁶⁰ Some other examples of Cu(I) chalcogenide clusters stabilized by phosphines highlighted in a review by Dehnen *et al.* are $[\text{Cu}_{12}\text{S}_6(\text{PEt}_3)_8]$, $[\text{Cu}_{12}\text{E}_6(\text{PEtPh}_2)_8]$ ($\text{E} = \text{S}, \text{Se}$), $[\text{Cu}_{12}\text{Te}_6(\text{PPh}_3)_8]$, $[\text{Cu}_{20}\text{S}_{10}(\text{PPh}_3)_8]$, $[\text{Cu}_{24}\text{S}_{12}(\text{PEt}_2\text{Ph})_{12}]$, $[\text{Cu}_{32}\text{Se}_{16}(\text{PPh}_3)_{12}]$, $[\text{Cu}_{52}\text{Se}_{26}(\text{PPh}_3)_{16}]$, $[\text{Cu}_{70}\text{Se}_{32}(\text{PEt}_3)]$, $[\text{Cu}_{146}\text{Se}_{73}(\text{PPh}_3)_{30}]$ etc.²⁴

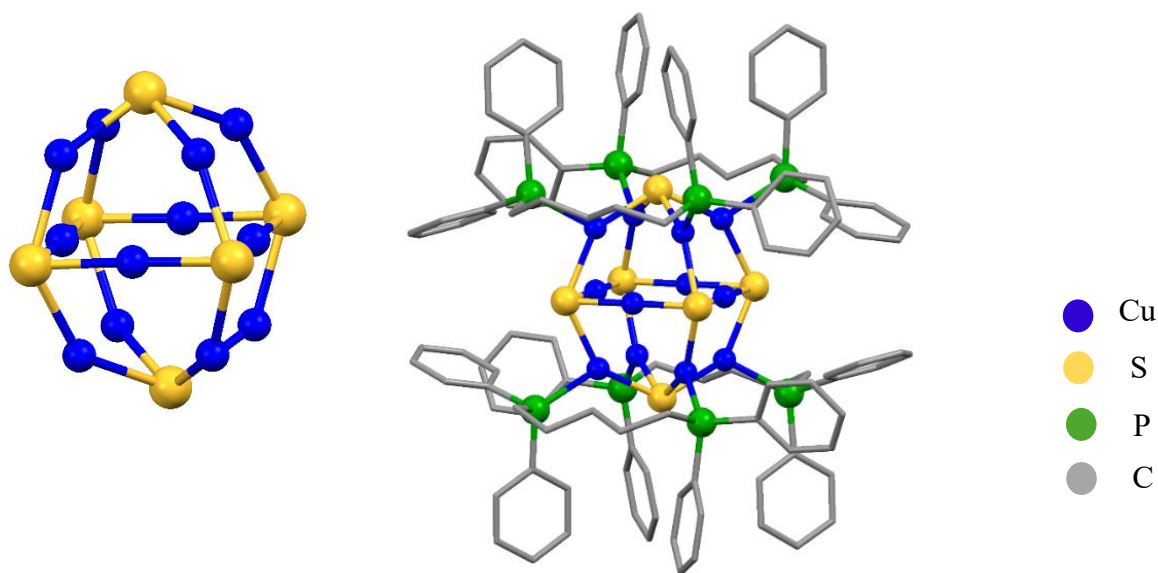


Figure 1.10: Molecular structure of “naked” $[\text{Cu}_{12}\text{S}_6]$ core (left) and $[\text{Cu}_{12}\text{S}_6(\text{dpppt})_4]$ (right). (H atoms have been omitted for clarity).⁶⁰

Au(I) chalcogenides are an interesting class of compounds known for their luminescent properties along with their known ability to exhibit aurophilic interactions, as a result, there is a greater

propensity to form self-assembled supramolecular assemblies.^{61–63} They are typically formed by multiple $[\text{Au}_3(\mu_3\text{-E})]^+$ subunits, therefore, many of the formed clusters being charged require counter ions (one or more anions). $[\text{Au}_{18}(\mu\text{-dpepp})_6(\mu_3\text{-S})_6]^{6+}$ (dpepp = *bis*(2-diphenylphosphinoethyl)phenylphosphine) is a prime example of gold(I) μ_3 -sulfido complex with $[\text{Au}_3(\mu_3\text{-S})]^+$ subunits as given in **Fig 1.11**.⁶⁴ The presence of aurophilic contacts which forms the ‘macrocycle’ is indicated by the Au(I)...Au(I) distances.⁶⁴

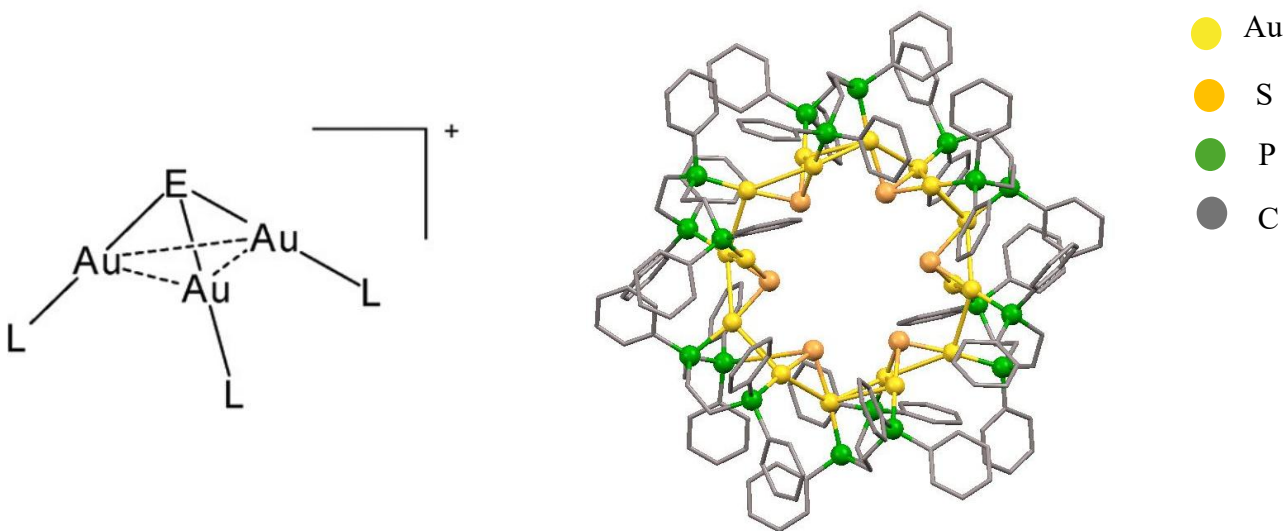


Figure 1.11: $[\text{Au}_3(\mu_3\text{-E})]^+$ subunit (left), molecular structure of $[\text{Au}_{18}(\mu\text{-dpepp})_6(\mu_3\text{-S})_6]^{6+}$ cation (right). (A water molecule sitting inside the cavity has been omitted for clarity). Figure adapted from ⁶⁴.

Fenske *et al.* introduced two examples of selenium bridged gold complex cations, (a) $[\text{Au}_{10}\text{Se}_4(\text{dppm})_4]\text{Br}_2$ (dppm = *bis*(diphenylphosphino) methane) and (b) $[\text{Au}_{18}\text{Se}_8(\text{dppe})_6]\text{X}_2$; (X = Cl, PF₆, BPh₄) (dppe = *bis*(diphenylphosphino) ethane).⁶⁵ The reaction of $\text{Se}(\text{SiMe}_3)_2$ with $[(\text{AuBr})_2(\text{dppm})]$ and $[(\text{AuCl})_2(\text{dppe})]$ leads to corresponding Au₁₀ and Au₁₈ clusters, respectively.

Further reactions of $[\text{Au}_{18}\text{Se}_8(\text{dppe})_6]\text{Cl}_2$ with KPF_6 or NaBPh_4 result in the formation of $[\text{Au}_{18}\text{Se}_8(\text{dppe})_6][\text{PF}_6]_2$ and $[\text{Au}_{18}\text{Se}_8(\text{dppe})_6][\text{BPh}_4]_2$, respectively. With the aid of electrospray ionization (ESI) mass spectrometry, the formation of $[\text{Au}_{18}\text{Se}_8(\text{dppe})_6]^{2+}$ dication species was confirmed.⁶⁵ Compared to Cu(I) and Ag(I), compounds of Au(I) are more likely to form low nuclearity clusters.⁶⁶ Cu(I) chalcogenide clusters can have nuclearities greater than 100 metal atoms for example $[\text{Cu}_{146}\text{Se}_{73}(\text{PPh}_3)_{30}]$.⁶⁷

1.6.1 NHC: a better alternative

The thermal instability associated with phosphine ligand coordination to cluster surfaces remained a challenge in exploring the high nuclearity coinage metal chalcogen compounds. This is highlighted in the work of Borecki and Corrigan, where they investigated a set of copper and silver trimethylsilylchalcogenolates with different phosphine ancillary ligands and addressed the thermal instability.⁶⁸ This instability could be attributed to the strength of M-phosphine interaction and in turn act as a limiting factor in stabilizing trimethylsilylchalcogenolates which can be used as precursors to metal-chalcogenide clusters. NHCs can trump phosphine ligands in terms of σ -donor ability and thus stabilizing metals more efficiently. Curiously, there have been only few reports on Cu(I) and Au(I) chalcogen compounds stabilized by NHCs as compared to phosphines.

The labile nature of phosphines often results in the formation copper(I) chalcogen compounds with thermal instability and poor solution processability making it difficult to store for longer periods and prevents it from forming ternary clusters. Inspired by this, Corrigan group expanded the library of coinage metal chalcogen compounds stabilized by phosphines to thermally stable class of NHC stabilized metal chalcogenides and chalcogenolates. In 2015, they synthesized a set of thermally stable copper chalcogenolate complexes by introducing the, NHC, 1,3-bis-(2,6-diisopropylphenyl)imidazolin-2-ylidene (IPr) as the first example.⁶⁹ It has the general formula,

$[(\text{IPr})\text{Cu}-\text{ESiMe}_3]$ where $\text{E} = \text{S}, \text{Se}, \text{Te}$ (**Fig.1.12**). Furthermore, the high melting points of these copper complexes indicated the exceptional thermal stability as compared to the phosphine counter part.

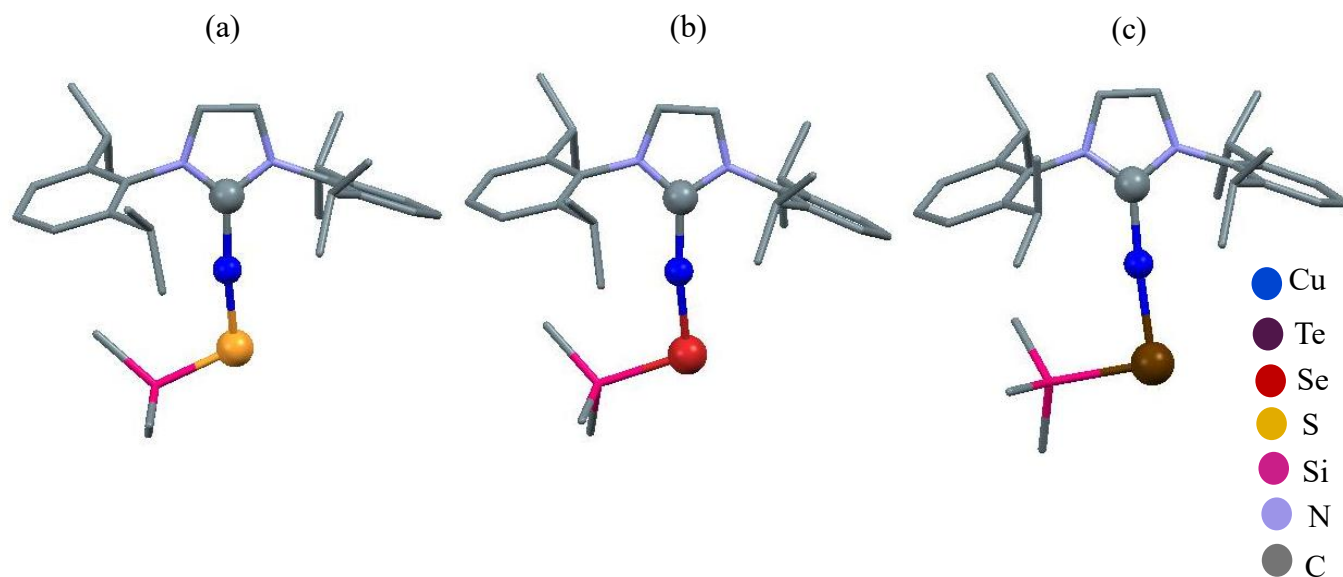


Figure 1.12: Molecular structure of (a) $[(\text{IPr})\text{Cu}-\text{SSiMe}_3]$, (b) $[(\text{IPr})\text{Cu}-\text{SeSiMe}_3]$ and (c) $[(\text{IPr})\text{Cu}-\text{TeSiMe}_3]$. (H atoms and solvents molecules have been omitted for clarity).⁶⁹

In 2017, the same group reported an exciting group of d^{10} -metal chalcogenide compounds protected by the same NHC ligand, IPr.²⁶ Gold(I) trimethylsilylchalcogenolate reagents were employed as precursors to form different octanuclear clusters, $[\text{Au}_4\text{M}_4(\mu_3\text{-E})_4(\text{IPr})_4]$ ($\text{M} = \text{Ag}, \text{Au}$; $\text{E} = \text{S}, \text{Se}, \text{Te}$) (**Fig. 1.13**). The silylchalcogenolate precursor showed exceptional stability due to the enhanced σ -donating ability of NHCs. Additionally, it allowed the fine-tuning of the photophysical properties of Au(I) chalcogenides by varying the M/E composition.

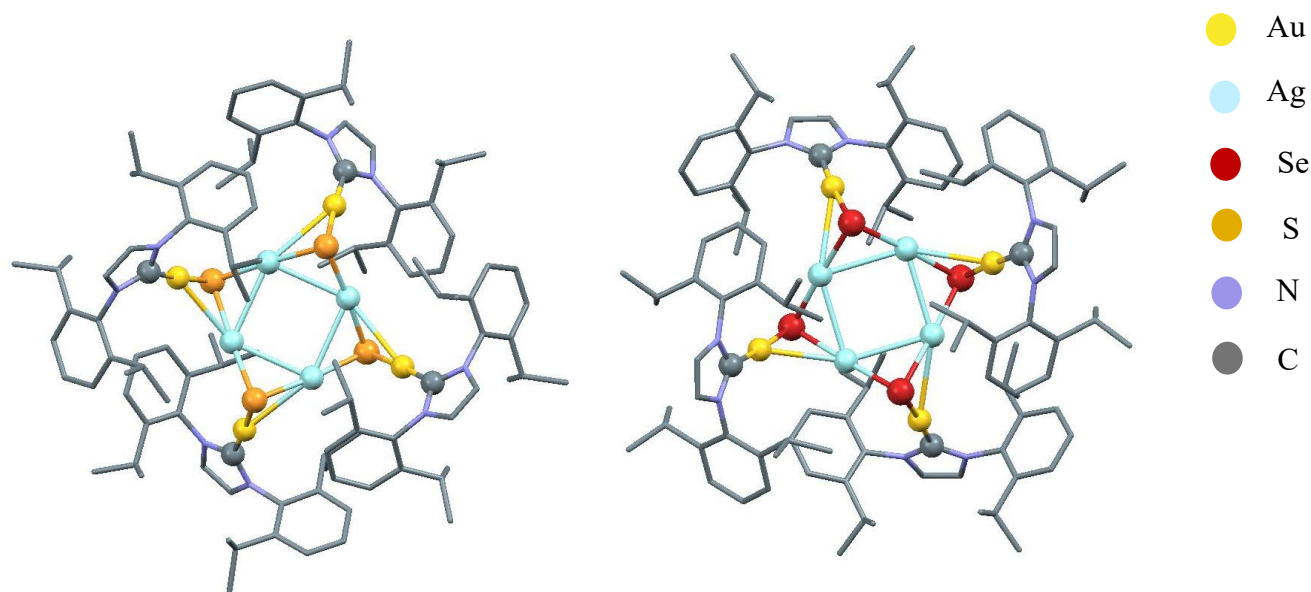


Figure 1.13: Molecular structure of $[\text{Au}_4\text{Ag}_4(\mu_3\text{-S})_4(\text{IPr})_4]$ (left) and $[\text{Au}_4\text{Ag}_4(\mu_3\text{-Se})_4(\text{IPr})_4]$ (right). (H atoms have been omitted for clarity).²⁶

The access to a wide variety of NHCs is crucial for the synthesis of ternary metal chalcogenide nanocluster architectures with tunable properties. Fard *et al.* for instance, successfully synthesized $[(\text{IPr})\text{Ag-ESiMe}_3]$ ($\text{E} = \text{S}, \text{Se}$) using the same ligand and $[(\text{iPr}_2\text{-bimy})\text{Cu-ESiMe}_3]$ ($\text{E} = \text{S}, \text{Se}$) complexes with a different NHC, $\text{iPr}_2\text{-bimy}$ ($\text{iPr}_2\text{-bimy} = 1,3\text{-bis}(2,6\text{-diisopropylphenyl})\text{imidazolin-2-ylidene}$).**(Fig.1.14)**.⁶⁹

The reaction of two equivalents of $[(\text{IPr})\text{Ag-SSiMe}_3]$ with mercuric(II) acetate ($[\text{Hg}(\text{OAc})_2]$) results in the formation of the first example of mixed silver–mercury–sulfide complex, $[\{(\text{IPr})\text{AgS}\}_2\text{Hg}]$ where two $(\text{IPr})\text{Ag-S}^-$ fragments were bonded to a central Hg^{II} . Interestingly, the reaction between $[(\text{iPr}_2\text{-bimy})\text{Cu-SSiMe}_3]$ and mercuric(II) acetate formed a high nuclearity cluster, $[(\text{iPr}_2\text{-bimy})_6\text{Cu}_{10}\text{S}_8\text{Hg}_3]$. The formation of two different products by changing surface ligands demonstrated the influence of ancillary ligands on the reaction chemistry. A key factor here is the

difference in ligand size and that can be explained by %V_{bur}. The %V_{bur} for smaller iPr₂-bimy is 27.9 but the larger IPr has a %V_{bur} of 44.5 (**Fig.1.14**).⁶⁹ Therefore, exploiting the stabilizing property of different NHC ligands in forming a wide variety of coinage metal chalcogen complexes and clusters is a very significant area in materials chemistry.³³

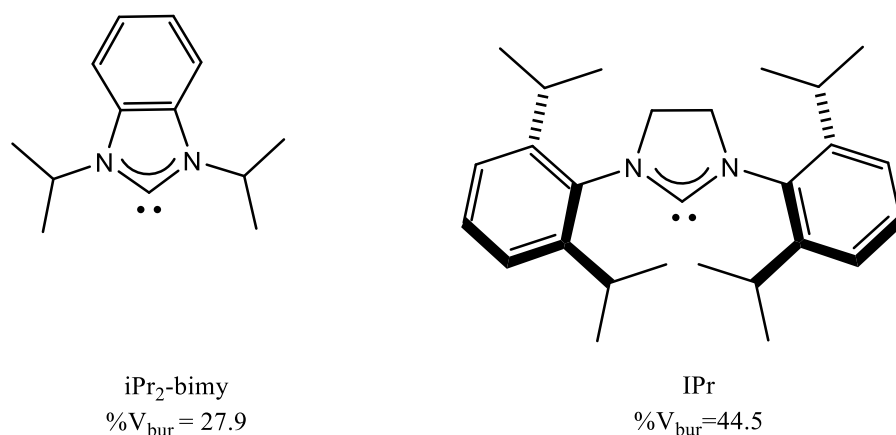


Figure 1.14: NHCs with different %V_{bur}.

1.6.2. Bidentate NHC ligands on the play: surface stabilization of coinage metal chalcogen clusters

Recently, bidentate NHC ligands are gaining increased scientific interest in stabilizing metallic nanoclusters.⁷⁰ The two coordinating sites in these ligands provide enhanced binding stability compared to monodentate ligands. This suggests that exploring the stabilizing properties of bidentate NHC is an interesting avenue in forming highly stable coinage metal chalcogen clusters.

In 2021, Crudden and co-workers reported a pioneer work on stabilizing highly luminescent Au₁₃ nanocluster with a bidentate NHC.⁷¹ The molecular formula of that cluster confirmed by single crystal X-ray crystallography is [Au₁₃(*bis*NHC^{Bn})₅Cl₂][Cl₃] (*bis*NHC^{Bn} = 1,1'-(dibenzyl)-3,3'-(1,2-xylylene)dibenzo[*d*]imidazol-2-ylidene) (**Fig.1.15**). Introduction of *bis*-benzimidazolylidene ligands bridged by aromatic linkers offered added advantage of many CH- π interactions which are

present in other Au₁₃ clusters.⁷² A fusion of properties obtained from a rigid bidentate NHC ligand and coinage metal chalcogenide is paving roads in the controlled synthesis of coinage metal chalcogenides stabilized by ancillary ligands and in fine tuning the photophysical properties.

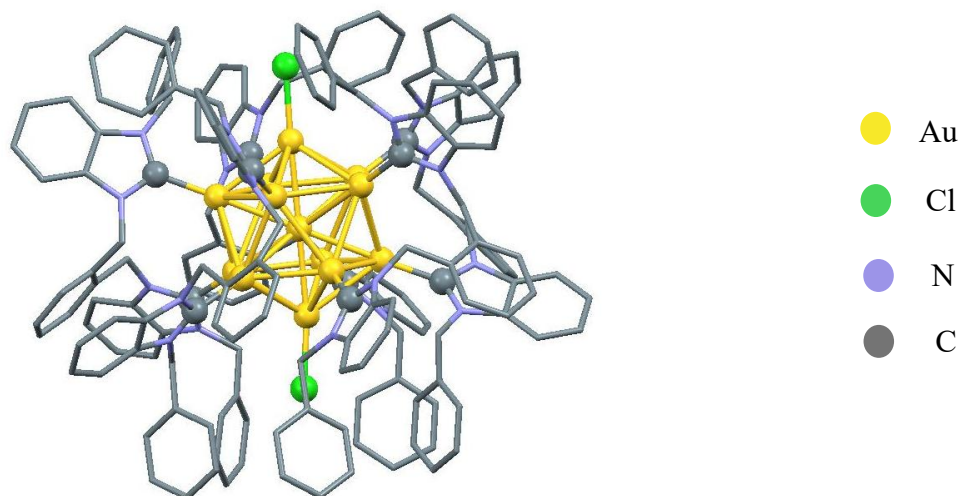


Figure 1.15: Molecular structure of $[\text{Au}_{13}(\text{bisNHC}^{\text{Bn}})_5\text{Cl}_2]\text{Cl}_3$ in the crystal. (anions and hydrogen atoms have been removed for clarity).⁷¹

The enhanced thermal stability of resulting Au₁₃ clusters is best highlighted in a recent report by Crudden *et al.* where they compared UV-vis spectra of that cluster with that of monotopic NHC derivatives⁷⁰. $[\text{Au}_{13}(\text{NHC}^{\text{Bn}})_9\text{Cl}_3]^{2+}$ (NHC^{Bn} = 1,3-Dibenzyl-1H-benzo[d]imidazol-2-ylidene) cluster stabilized by monotopic NHC ligand with benzyl (Bn) wingtips shows a considerable decline in key signal after heating in acetonitrile (ACN) at 70 °C for 20 h⁷² (**Fig.1.16**). However, UV-vis spectral studies of $[\text{Au}_{13}(\text{bisNHC}^{\text{Bn}})_5\text{Cl}_2]^{3+}$ ($\text{bisNHC}^{\text{Bn}}$ = 1,1'-(dibenzyl)-3,3'-(1,2-xylylene)dibenzo[d]imidazol-2-ylidene) cluster stabilized by the bidentate NHC shows no evidence for decomposition even after heating at 60 °C for 72 h.⁷¹

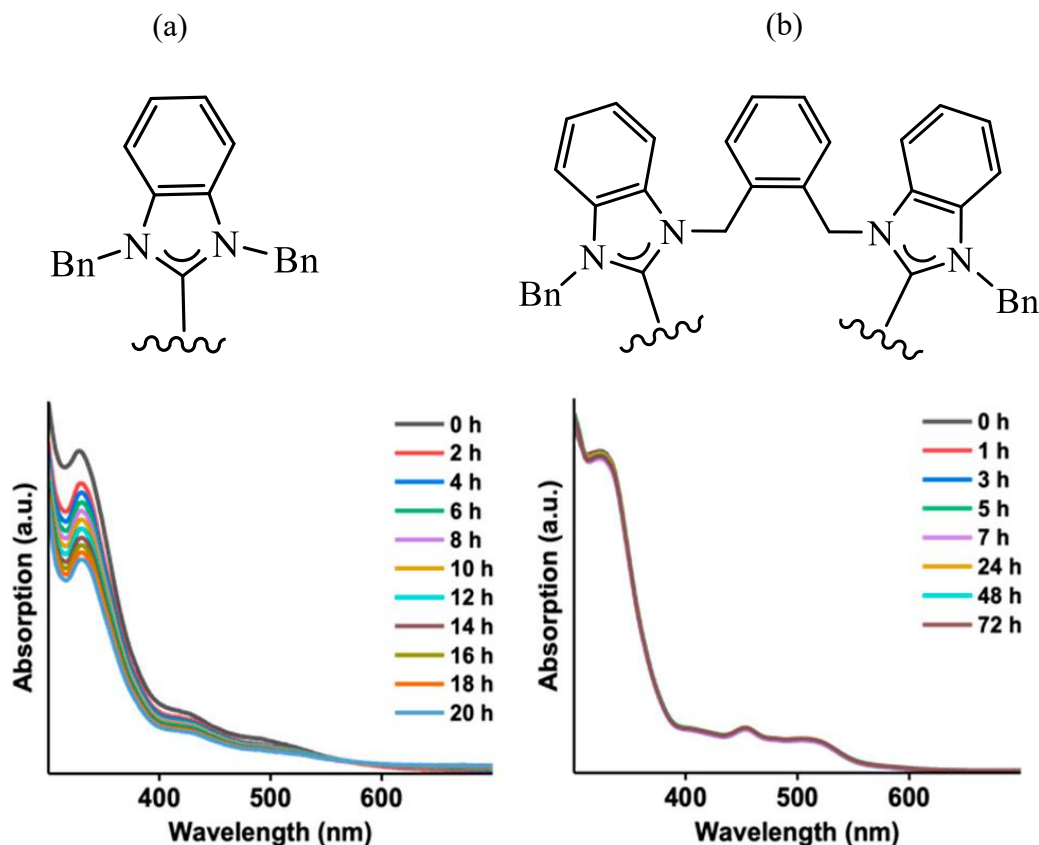


Figure 1.16: UV-vis absorption spectra of (a) $[\text{Au}_{13}(\text{NHC}^{\text{Bn}})_9\text{Cl}_3]^{2+}$ and (b) $[\text{Au}_{13}(\text{bisNHC}^{\text{Bn}})_5\text{Cl}_2]^{3+}$ clusters heated in ACN. Reprinted from

1.7 Scope of Thesis

This thesis focuses on the work conducted on incorporating a rigid bidentate NHC, onto Cu(I) and Au(I) chalcogen (E= Se) clusters to expand the library of group 11 metal chalcogen clusters stabilized by NHCs. The enhanced binding stability of the bidentate NHC ligand, 1,1'-(dibenzyl)-3,3'-(1,2-xylylene)dibenzo[*d*]imidazol-2-ylidene is explored in forming gold and copper chalcogen (E= Se) compounds. Chapter 2 focuses on the synthesis and characterization of Cu(I) and Au(I) chalcogen (E = Se) clusters stabilized by the same bidentate NHC ligand. Chapter 3 summarizes the results from chapter 2 and suggests future directions for projects involving bidentate NHCs to stabilize group 11 metal selenium compounds.

Chapter 2

2.0 Copper (I) and Gold (I) chalcogen clusters with bidentate NHC ligand

2.1 Introduction

Group 11 metal chalcogen clusters have been widely investigated due to their diverse dimensionalities, varying metal core sizes, tunable photophysical properties etc.^{11,24,73} These tunable photophysical properties make them promising candidates for a wide range of applications especially in optoelectronics, bioimaging and as light emitting materials.^{74,75} These clusters are also notable for their structural diversity, long-lived excited states and, protecting ligand-dependant luminescence.¹¹ It is possible to modify the electronic structure of group 11 metal chalcogen clusters by altering the organic ligands resulting in changes to their HOMO-LUMO gap.⁷⁶ This tunability makes such clusters attractive targets for incorporation into everyday electronics particularly, in applications such as organic light emitting diodes (OLEDs).^{60,77}

Cu(I), Ag(I) and Au(I) exhibit different structural features due to their individual preferences for various coordination modes and differing tendencies to form metallophilic interactions. The lighter d^{10} metals, Cu(I) and Ag(I) can achieve four coordinate geometries with different ligands, while the Au(I), being heavier, typically adopts a coordination number of two. As a result, chalcogen complexes of Au(I) form low nuclearity clusters more often than the Cu(I) or Ag(I) analogues.⁶⁶

The complexes of gold in +1 oxidation state have been receiving increased scientific interest primarily due their ability to exhibit secondary bonds known as aurophilic interactions. The strength of Au(I)...Au(I) interactions (7-11 kcal/mol) is comparable to that of hydrogen bonding.^{78,79} It was recognized that d^{10} - d^{10} attraction strengthened by relativistic effects is

correlated to photoluminescence in Au(I) complexes.^{51,80} Several Au(I) chalcogenide clusters show interesting luminescent properties for example, $[\text{Au}_4\text{M}_4(\mu_3\text{-E})_4(\text{IPr})_4]$ ($\text{M} = \text{Ag}, \text{Au}$; $\text{E} = \text{S}, \text{Se}, \text{Te}$; $\text{IPr} = 1,3\text{-bis}(2,6\text{-diisopropylphenyl})\text{imidazole-2-ylidene}$).²⁶ These clusters are phosphorescent in solid state and in solution state with emission energies that depend on the selection of metal/chalcogen composition.

Au(I) chalcogenides stabilized by phosphine ancillary ligands form clusters typically based on multiple $[(\mu_3\text{-E})\text{Au}_3]^+$ units.⁸¹ Numerous clusters with different sizes and geometries have been reported by varying the Tolman cone angle, denticity and functional groups in the stabilizing phosphines.^{82–86} However, there have been only few reports on coinage metal chalcogen clusters with N-heterocyclic carbenes (NHCs). In this context, a rigid bidentate NHC ligand has been selected and incorporated to the coinage metal chalcogenides ($\text{M} = \text{Au}$; $\text{E} = \text{Se}$).

Similar to the coinage metal chalcogenides, group 11 d^{10} metal chalcogenolates (M-ER , $\text{E} = \text{S}, \text{Se}, \text{Te}$; $\text{R} = \text{organic substituent}$) have received significant attention as they are endowed with wide range of structural, chemical and photophysical properties.¹¹ The combination of group 11 metals ($\text{Cu}, \text{Ag}, \text{Au}$) with chalcogenolates is a promising field in light emitting materials owing to the tunability of their electronic, conductive and photophysical properties.^{57,87} Both coinage metal chalcogenides and chalcogenolates can be readily prepared from silylated reagents, $\text{E}(\text{SiMe}_3)$ and RESiMe_3 , ($\text{R} = \text{organic substituent}$, $\text{E} = \text{S}, \text{Se}, \text{Te}$). The reactions of ligand protected metal complexes (LMX , $\text{L} = \text{organic protecting ligand}$, $\text{M} = \text{Cu}, \text{Ag}, \text{Au}$, $\text{X} = \text{leaving group: OAc, OTf, Cl}$) ($\text{OTf} = \text{trifluoromethanesulfonate}$) with $\text{E}(\text{SiMe}_3)$ or RESiMe_3 lead to a corresponding metal chalcogenide or chalcogenolate core, respectively.^{11,88,89} These reactions are driven by the formation of X-SiMe_3 byproducts.¹⁶ The size and structure of coinage metal chalcogenolate clusters can be selectively targeted by altering the organic moiety in RE^- or by changing the steric

hindrance of the organic moiety bonded to the chalcogen (E= S, Se, Te).^{77,84} In addition, attachment of an organic substituent plays a crucial role in providing stability and prevents the formation of undesirable bulk M_2E by products.^{90–92}

Phosphine ligands are one of the most common protecting ligand in d^{10} - coinage metal chalcogen compounds. However, recent works from Corrigan lab indicated the better stability of group 11 metal chalcogen compounds with monodentate NHCs and CAACs (cyclic (alkyl)(amino) carbenes), due to the greater σ -donating ability of these carbene based ligands.^{26,27} Logically, incorporating a bidentate NHC provides more binding stability to the cluster than monodentate NHC ligands. The two carbene centres in bidentate NHC stabilize the metal centers efficiently. Based on this, a rigid bidentate NHC was selected given below. Crudden and co-workers reported a pioneer work on stabilizing highly luminescent Au_{13} nanocluster with this bidentate NHC.⁷¹ Interestingly, the UV-Vis spectral studies of this Au_{13} clusters $[Au_{13}(bisNHC^{Bn})_5Cl_2]^{3+}$ ($bisNHC^{Bn}$ = 1,1'-(dibenzyl)-3,3'-(1,2-xylylene)dibenzo[d]imidazol-2-ylidene) cluster shows no evidence for decomposition even after heating at 60 °C for 72 h compared to the monodentate NHC, indicating the better thermal stability of $bisNHC^{Bn}$ in the cluster.⁷⁰

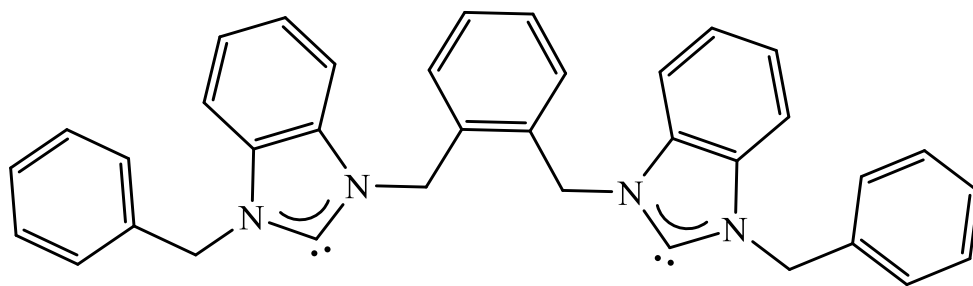


Figure 2.1: 1,1'-(dibenzyl)-3,3'-(1,2-xylylene)dibenzo[d]imidazol-2-ylidene ($bisNHC^{Bn}$).⁷¹

Herein, the incorporation of the bidentate NHC 1,1'-(dibenzyl)-3,3'-(1,2-xylylene)dibenzo[*d*]imidazol-2-ylidene (*bis*NHC^{Bn}) (Fig. 2.1) onto Au(I) and Cu(I) centres for the formation of chalcogen clusters is reported. [(AuOAc)₂(*bis*NHC^{Bn})] (**2.1**) represents an excellent starting point for the preparation of Au(I) chalcogen clusters stabilized by *bis*NHC^{Bn}. [(AuOAc)₂(*bis*NHC^{Bn})] (**2.1**) was synthesized by stirring 1.0 equivalents of [(AuCl)₂(*bis*NHC^{Bn})] with 2.5 equivalents of AgOAc, resulting in the NHC ligated metal acetate complex.⁹³ Se(SiMe₃)₂ and PhSeSiMe₃ were subsequently introduced to the solutions of (**2.1**) to form [Au₆Se₂(*bis*NHC^{Bn})₃]²⁺ (**2.2**) and [(AuSePh)₂(*bis*NHC^{Bn})] (**2.3**), respectively.

For targeting Cu(I) chalcogen clusters with *bis*NHC^{Bn}, a new complex [(CuCl)₂(*bis*NHC^{Bn})] (**2.4**) was prepared to access copper selenide (**2.5**) and copper selenolate (**2.6**) containing the *bis*NHC^{Bn}. [(CuCl)₂(*bis*NHC^{Bn})] (**2.4**) was synthesized by refluxing a mixture of 2.0 equivalents of CuCl and 1.0 equivalent [*bis*NHC^{Bn}H₂]Cl₂ in the presence of triethyl amine in acetonitrile (ACN).

2.2 Results and Discussion

2.2.1 Synthesis and Characterization of [Au₆Se₂(*bis*NHC^{Bn})₃]²⁺ (**2.2**) and [(AuSePh)₂(*bis*NHC^{Bn})] (**2.3**)

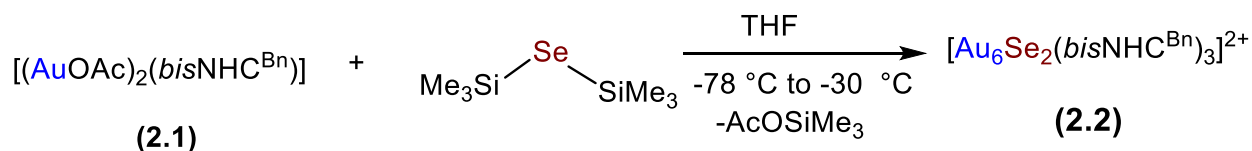
Given that ligand (phosphine or NHC usually) protected group 11 metal complexes react with chalcogen reagents with -SiMe₃ moieties^{11,69,73,94,95}, [(AuOAc)₂(*bis*NHC^{Bn})] (**2.1**) represents the starting point to prepare gold chalcogenide/chalcogenolate clusters which contain *bis*NHC^{Bn} ligand. This new gold complex (**2.1**) was prepared by the metathesis reaction between AgOAc and [(AuCl)₂(*bis*NHC^{Bn})].⁷¹ The synthesis of compounds (**2.2**) and (**2.3**) was conducted by adding 1.0 equivalent of Se(SiMe₃)₂ and 2.0 equivalents of PhSeSiMe₃ to solutions of [(AuOAc)₂(*bis*NHC^{Bn})] (**2.1**), respectively in THF.

The synthesis of **(2.2)** and **(2.3)** was initially attempted with the known starting gold-chloride- $[(\text{AuCl})_2(\text{bisNHC}^{\text{Bn}})]^{71}$ resulting in either incomplete reactions or formation of undesired products such as reduced gold ($\text{Au}(0)$). The next logical step was to prepare this new complex, $[(\text{AuOAc})_2(\text{bisNHC}^{\text{Bn}})]$ **(2.1)** with a better leaving group. The metathesis reaction between AgOAc and $[(\text{AuCl})_2(\text{bisNHC}^{\text{Bn}})]$ in DCM formed the desired $[(\text{AuOAc})_2(\text{bisNHC}^{\text{Bn}})]$ **(2.1)** and AgCl by-product.⁹³ The precipitated AgCl was removed by filtering the reaction solution over Celite. The volatiles were removed *in vacuo* yielding **(2.1)** in 99% yield. The formation of $[(\text{AuOAc})_2(\text{bisNHC}^{\text{Bn}})]$ **(2.1)** was confirmed by an indicative peak from -OAc group in the ^1H NMR spectrum ($\delta = 2.00$ ppm) of **(2.1)** in CDCl_3 compared to that of $[(\text{AuCl})_2(\text{bisNHC}^{\text{Bn}})]$. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **(2.1)** shows evidence for the OAc group with resonances at 174.03 ppm (CH_3COO) and 23.98 ppm (CH_3COO). The $\text{Au}-\text{C}_{\text{carbene}}$ signal was observed at 177.31 ppm in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **(2.1)**. It was then further confirmed with the aid of ATR-FTIR, showing a characteristic band at 1606.5 cm^{-1} attributed to the $\text{C}=\text{O}$ stretch from -OAc group.⁹³ Full characterization details are found in the Experimental.

2.2.1.1 Synthesis and Characterization of $[\text{Au}_6\text{Se}_2(\text{bisNHC}^{\text{Bn}})_3]^{2+}$ **(2.2)**

(2.2) was synthesized by adding 1.0 equivalent of $\text{Se}(\text{SiMe}_3)_2$ to $[(\text{AuOAc})_2(\text{bisNHC}^{\text{Bn}})]$ **(2.1)** at $-78\text{ }^\circ\text{C}$ in THF (**Scheme 2.1**). As the reaction warmed to $-30\text{ }^\circ\text{C}$, reactions changed from a white suspension into a clear colorless solution. The starting material, $[(\text{AuOAc})_2(\text{bisNHC}^{\text{Bn}})]$ **(2.1)** was not luminescent in the solid state or as a solution in THF, but the reaction solution for the formation of **(2.2)** displayed a green luminescence at $-30\text{ }^\circ\text{C}$ when illuminated with a handheld UV lamp ($\lambda_{\text{exc}} = 365\text{ nm}$). Reaction solutions stored at $-30\text{ }^\circ\text{C}$ showed no additional changes over a period of 3 days. Layering reaction solutions with diethyl ether at $-30\text{ }^\circ\text{C}$, led to the formation of an off-white

solid. This solid was attempted to be solubilized in CDCl_3 , CD_2Cl_2 , CD_3CN , $\text{C}_5\text{D}_5\text{N}$, C_7D_8 and $\text{DMSO}-d_6$, however it was only sparingly soluble in these solvents.



Scheme 2.1: Synthetic scheme of gold chalcogenide complex **(2.2)**.

Low-resolution electrospray ionization mass spectrometry (LR-ESI-MS) analysis (positive mode) was performed by preparing acetonitrile-dichloromethane (1:1 v/v) dispersions of **(2.2)** (*ca.* 0.1 mg/mL). The mass spectrum of the off-white solid displayed a rather limited distribution of a species with predominant signal at $m/z = 1448.25$ (**Fig 2.2**). When the mass spectrum was analysed, m/z peak separation indicated a 2+ charge for this complex which is characteristic of a known $[\text{Au}_6\text{Se}_2]^{2+}$ framework⁹⁴ possibly from $[\text{Au}_6\text{Se}_2(\text{bisNHC}^{\text{Bn}})_3]^{2+}$ **(2.2)**. The peak at $m/z = 1487.50$ indicate a species with a +1 charge state which could be attributed to $[\text{Au}_3\text{SeC}_{57}\text{H}_{48}\text{N}_6]^+$, where the $\text{C}_{57}\text{H}_{48}\text{N}_6$ constitutes a $\text{bisNHC}^{\text{Bn}}$ ($\text{C}_{36}\text{H}_{30}\text{N}_4$) along with a monodentate NHC^{Bn} ($\text{C}_{21}\text{H}_{18}\text{N}_2$) formed from the fragmentation of another $\text{bisNHC}^{\text{Bn}}$ ligand. This type of $[\text{Au}_3\text{Se}]^+$ based subunits are highly expected from gold selenide clusters.^{96,97}

There is a signal at $m/z = 1787.25$, which can be assigned to a formula $[\text{Au}_3\text{Se}_2(\text{bisNHC}^{\text{Bn}})_2]^+$, however the existence of this species has not been reported previously and the most common gold selenide subunit is $[\text{Au}_3\text{Se}]^+$. In the observed $[\text{Au}_3\text{Se}_2]$ based subunit, the overall charge calculated is -1 ($\text{Au} = +1$ and $\text{Se} = -2$). This questions existence of a negative species in ESI positive mode. A possibility here might be one of the Au oxidizes to +3 oxidation state resulting in an overall +1

charge in $[\text{Au}_3\text{Se}_2]$ state to be detected in ESI positive mode. The isotopic pattern of $[\text{Au}_3\text{Se}_2(\text{bisNHC}^{\text{Bn}})_2]^+$ matches with the simulated pattern (calculated = 1787.23, found = 1787.25), therefore we cannot entirely neglect the existence of $[\text{Au}_3\text{Se}_2]^+$ based species (**Fig. 2.3**). A less intense signal at $m/z = 1939.16$ ($z = 1$) could not be assigned to a structure, but the isotopic pattern suggest that this species contains more than one selenium atom. The full mass spectrum is attached in the **Appendix** in *Figures S2.19*. Overall, the limited solubility of reaction products limited more complete characterization.

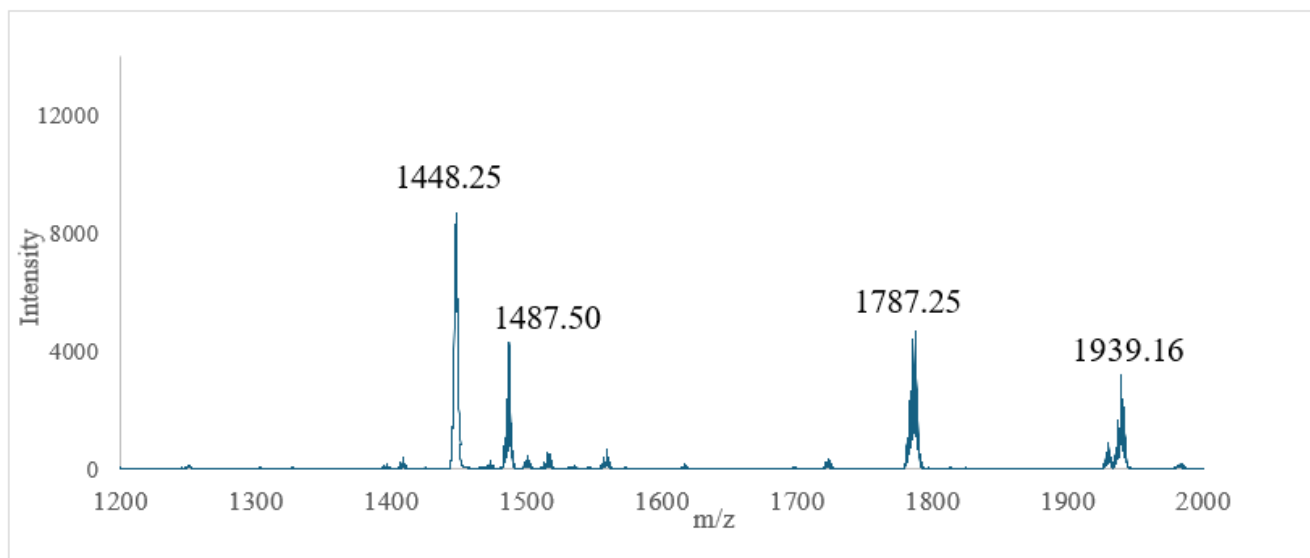


Figure 2.2: Mass spectrum (ESI positive mode) of the off-white solid material obtained from the reaction between $[(\text{AuOAc})_2(\text{bisNHC}^{\text{Bn}})]$ (**2.1**) and $\text{Se}(\text{SiMe}_3)_2$.

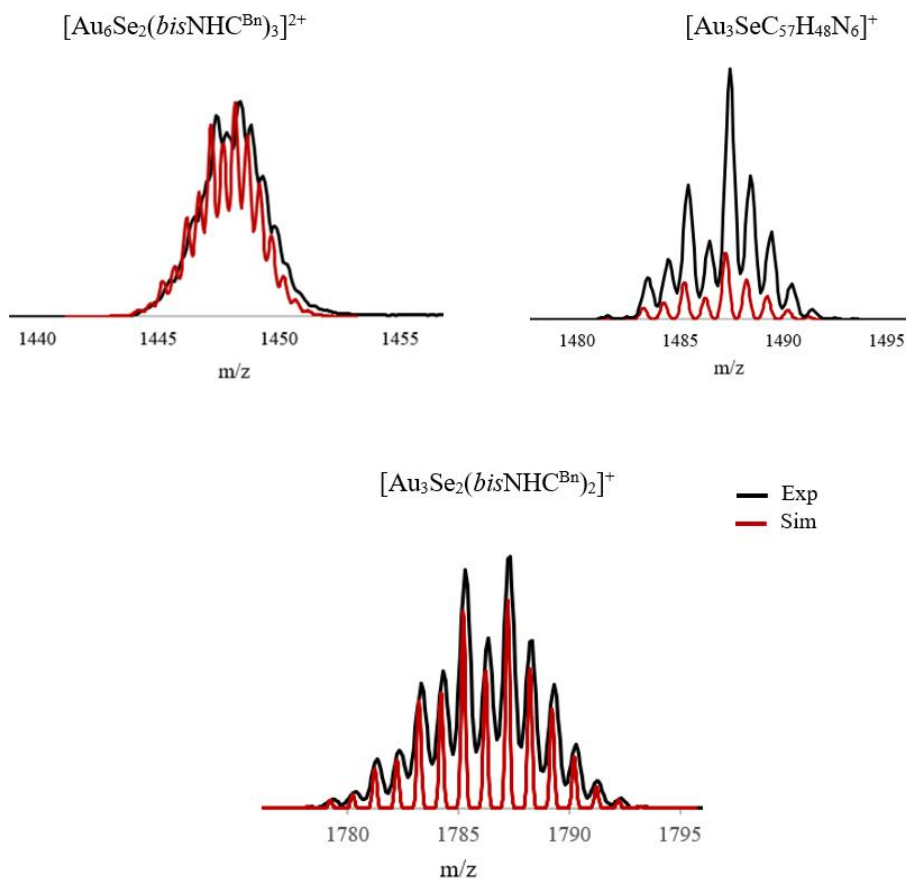


Figure 2.3: Experimental and simulated isotopic patterns of different fragments.

Given that Au(I) chalcogenides have a greater propensity to form clusters by multiple $[\text{Au}_3\text{E}]^+$ subunits, the selenide atoms within **(2.2)** could possibly bridge three gold centres. Villacampa and Yam reported many of gold clusters with this $(\text{Au}_3\text{E})^+$ subunit. Some examples of such clusters are $[\text{E}(\text{AuPPh}_2\text{CH}_2\text{-CH}_2\text{py})_3]\text{BF}_4$, $[(\text{E}(\text{AuPPh}_2\text{py})_3)]\text{BF}_4$ and $[\text{Au}_6(\text{Ph}_2\text{PN}(\text{CH}_3)\text{PPh}_2)(\mu_3\text{-S})]\text{Cl}_2$.^{96,97} A similar cluster, $[\text{Au}_6(\mu_3\text{-Se})_2(\mu\text{-dbfdp})_3]^{2+}$ (dbfdp= 4,6-bis(diphenylphosphino)dibenzofuran)) stabilized by a bidentate phosphine ligand was recently reported.⁹⁴ In this cluster, two individual $(\text{Au}_3\text{Se})^+$ subunits are bridged by suggested aurophilic interactions between Au(1) and Au(1) and

two P3 atoms in the DBFDP ligand links two gold (I) centres Au(3) and Au(3), one each from the individual $(\text{Au}_3\text{Se})^+$ subunits (**Fig. 2.4**).

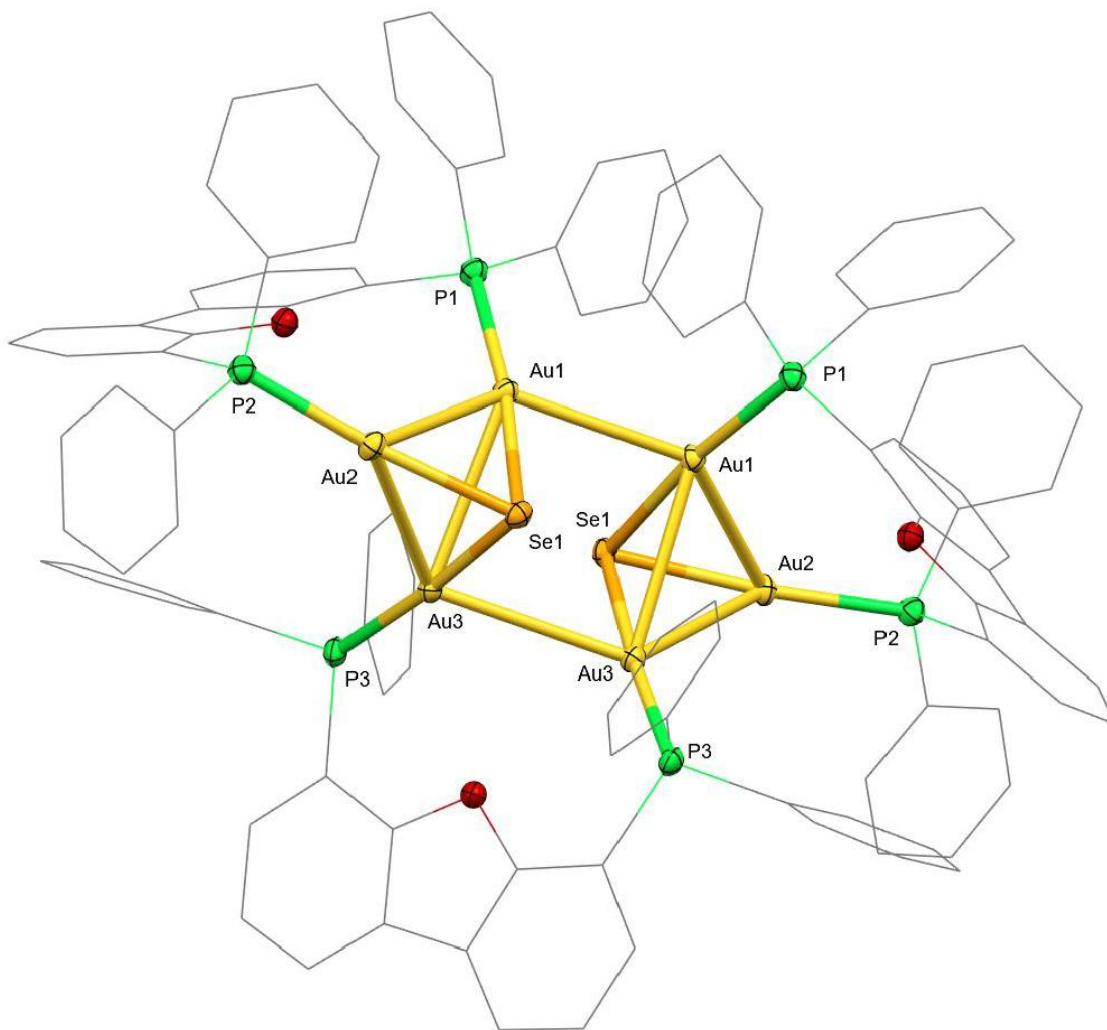


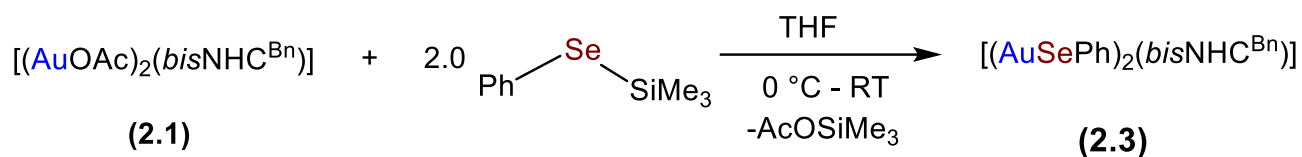
Figure 2.4: Molecular structure of $[\text{Au}_6(\mu_3\text{-Se})_2(\mu\text{-dbfdp})_3]^{2+}$ unit in the crystal (Au – Se: 2.432(1) Å – 2.477(1) Å, Au...Au: 3.0473(8) Å – 3.1844(9) Å) (H atoms and OTf anions omitted for clarity).⁹⁴

The IR spectrum of **(2.2)** displayed a weak -OAc peak (C=O stretch) at around 1600 cm^{-1} compared to the starting to $[(\text{AuOAc})_2(\text{bisNHC}^{\text{Bn}})]$ **(2.1)** complex.⁹³ This suggests the presence of AcO^- as counter ions which agrees with the synthetic conditions as well. Therefore, the complete cluster

formula is tentatively assigned as $[\text{Au}_6\text{Se}_2(\text{bisNHC}^{\text{Bn}})_3](\text{OAc})_2$. The IR spectrum is attached in the **Appendix** in *Figures S2.11*.

2.2.1.2 Synthesis and Characterization of $[(\text{AuSePh})_2(\text{bisNHC}^{\text{Bn}})]$ (2.3)

The synthesis of complex **(2.3)** was carried out by adding 2 equivalents of PhSeSiMe_3 to a solution of $[(\text{AuOAc})_2(\text{bisNHC}^{\text{Bn}})]$ (**(2.1)**) in THF at 0 °C. $[(\text{AuOAc})_2(\text{bisNHC}^{\text{Bn}})]$ was not totally soluble in THF, however upon the addition of PhSeSiMe_3 , it formed a clear yellow solution indicating the higher solubility of product **(2.3)**. The reaction is highlighted in **Scheme 2.2** below.



Scheme 2.2: Synthetic scheme of gold chalcogenolate complex **(2.3)**.

The reaction proceeds from a cloudy colorless solution to a light-yellow clear solution instantaneously after adding PhSeSiMe_3 and changed to a clear yellow solution at room temperature. The reactions were monitored with TLC (mobile phase = 1:1 THF:hexane) and they showed two products (a minor and major) after a day of stirring at RT. After precipitating out **(2.3)** with heptane, evidence for the minor product was no longer there. The yellow solid that precipitated displayed a bright red luminescence at 77 K in the solid state. The reaction completion was further confirmed with the aid of ATR-FTIR spectroscopy. The absence of a characteristic band (C=O stretch in -OAc) at around 1606 cm^{-1} in the IR spectrum of **(2.3)** indicated the displacement of the OAc moieties.⁹³

The mass spectrum of **(2.3)** shows an interesting peak at $m/z = 1069.16$ (**Fig. 2.5**). When the mass spectrum was analysed, peak separation indicated a +1 charge. This peak could be attributed to

$[\text{Au}_2(\text{SePh})(\text{bisNHC}^{\text{Bn}})]^+$ species formed from $[(\text{AuSePh})_2(\text{bisNHC}^{\text{Bn}})]$ (**2.3**) by the loss of the phenyl selenolate ligand. There were no peaks corresponding to the fragments of (**2.1**) confirming the successful reaction completion.

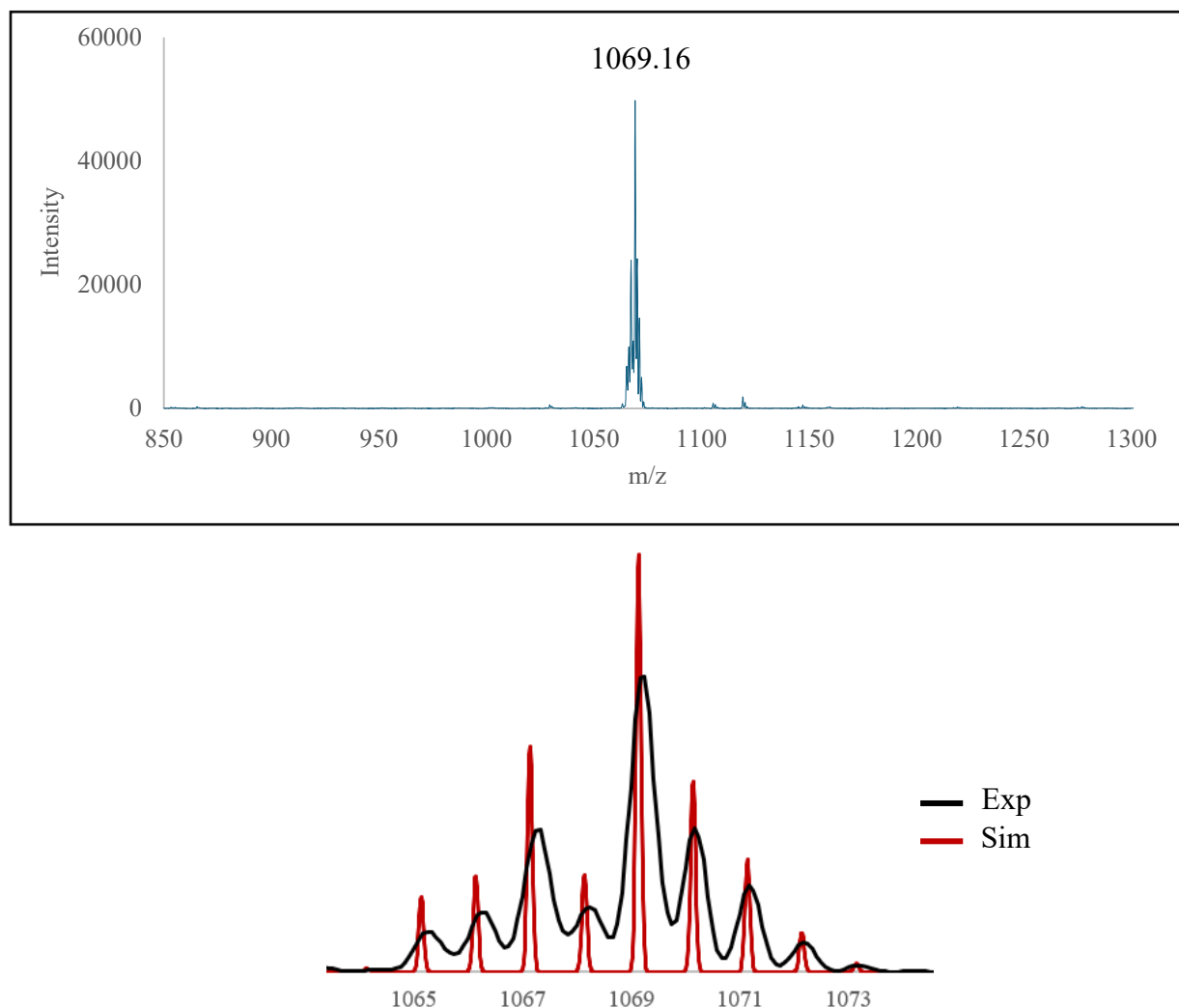
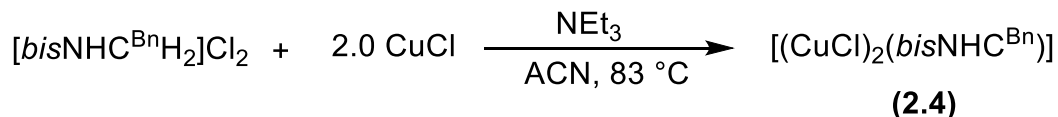


Figure 2.5: Mass spectrum (ESI positive mode) of $[(\text{AuSePh})_2(\text{bisNHC}^{\text{Bn}})]$ (**2.3**) obtained from the reaction between $[(\text{AuOAc})_2(\text{bisNHC}^{\text{Bn}})]$ (**2.1**) and PhSeSiMe_3 (top), simulated and experimental isotopic pattern of $[\text{Au}_2(\text{SePh})(\text{bisNHC}^{\text{Bn}})]^+$ (bottom).

2.2.2 Attempted synthesis and Characterization of copper selenides (2.5) and copper selenolates (2.6) stabilized by *bisNHC*^{Bn}

A new of complex, [(CuCl)₂(*bisNHC*^{Bn})] (**2.4**) was prepared to target copper selenide and copper selenolate with *bisNHC*^{Bn}. It was prepared by the reaction of Cu(I)Cl with [*bisNHC*^{Bn}H₂]₂Cl₂ in the presence of triethyl amine (Et₃N) as given in **Scheme 2.3**. The yellow solid formed was then washed with ACN, washed with water followed by washing with a mixture of 1:3 MeOH-diethyl ether. The volatiles were removed *in vacuo* yielding the desired product (**2.4**) as an off-white powder.



Scheme 2.3: Synthetic scheme for the preparation of [(CuCl)₂(*bisNHC*^{Bn})] (**2.4**).

The off-white solid isolated was mainly characterized with the aid of mass spectrometry (ESI positive mode). Mass spectrum of (**2.4**) shows a predominant peak at *m/z*= 617.16 corresponding to the [(CuCl)(*bisNHC*^{Bn}) + H]⁺ species formed by the loss of a CuCl and protonation of one of the carbene centers (**Fig 2.6**). Other minor peaks (a), (b) and (c) are identified and follows, peak (a) at *m/z*= 491.16 is attributed to the [C₂₉H₂₃N₄Cu+H]⁺ species resulting from the fragmentation of the ligand at one of the wingtips. The peak (b) at *m/z*= 535.33 is ascribed to the oxidized form of ligand [(*bisNHC*^{Bn}) + O + H]⁺. The peak (c) at *m/z*= 581.25 correspond to [Cu(*bisNHC*^{Bn})]⁺ species. The full mass spectrum is attached in the **Appendix** in *Figures S2.21*.

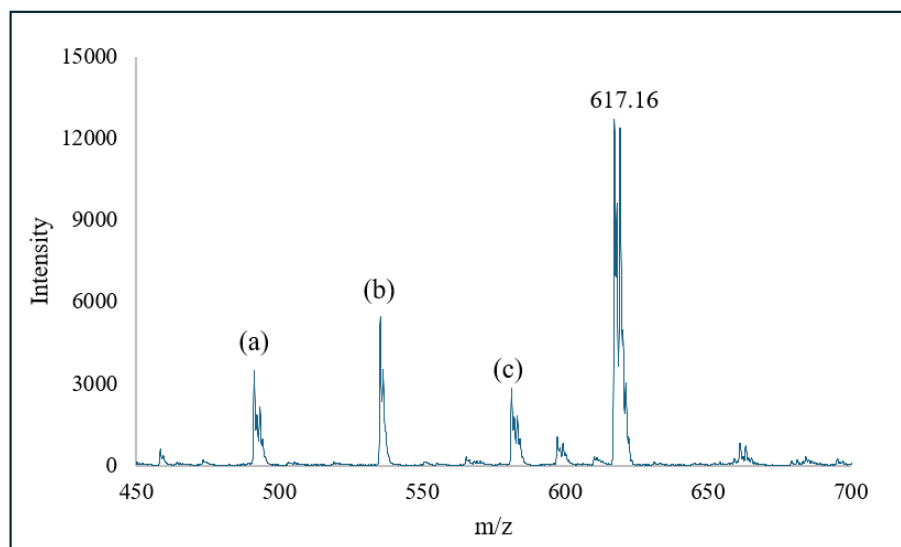


Figure 2.6: Mass spectrum (ESI positive mode) of $[(\text{CuCl})_2(\text{bisNHC}^{\text{Bn}})]$ (**2.4**) obtained from the reaction between $[\text{bisNHC}^{\text{Bn}}\text{H}_2]\text{Cl}_2$ and CuCl .

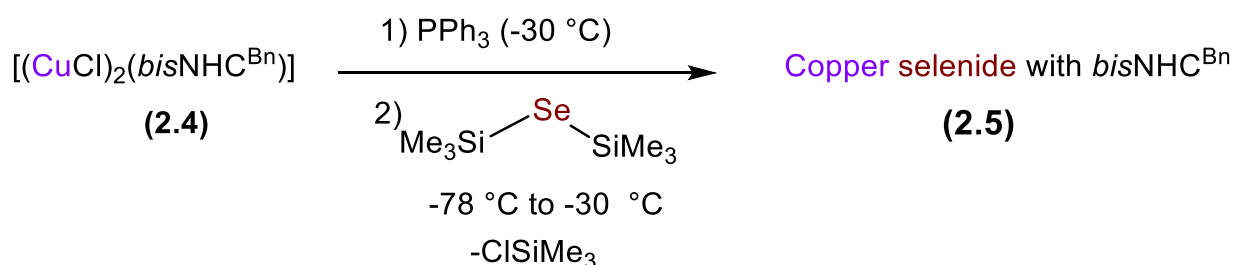
^1H NMR spectrum of (**2.4**) in $\text{DMSO}-d_6$ shows the disappearance of a singlet peak at around 10 ppm (benzimidazolium protons, 2H) compared to the spectrum of the starting benzimidazolium salt. This indicates the successful deprotonation in $[\text{bisNHC}^{\text{Bn}}\text{H}_2]\text{Cl}_2$ and the formation of $\text{Cu}-\text{C}_{\text{carbene}}$ bonds. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of (**2.4**) shows a peak at 186.88 ppm, which has been ascribed to the $\text{Cu}-\text{C}_{\text{carbene}}$ signal. Full characterization details are found in the Experimental.

Scanning electron microscopy with energy dispersive X-ray (SEM-EDX) spectroscopic analysis of (**2.4**) shows a 1:1 atomic ratio of copper to chlorine. This agrees with the expected ratio between copper and chlorine in $[(\text{CuCl})_2(\text{bisNHC}^{\text{Bn}})]$ (**2.4**). The full SEM-EDX characterization is attached in the **Appendix** in *Figures S2.16*.

2.2.2.1 Attempted synthesis of copper selenide clusters with *bisNHC*^{Bn} (2.5)

The reactions of ligand protected copper complexes with $\text{Se}(\text{SiMe}_3)_2$ are typically performed at low temperature to ensure the kinetic control and to avoid the formation of thermodynamically favoured bulk Cu_2Se .⁷³ These reactions of starting CuX ($\text{X} = \text{Cl}, -\text{OAc}$) complexes with $\text{Se}(\text{SiMe}_3)_2$ generally progresses with a gradual colour change from colorless to yellow to orange to brown upon warming from -78°C to room temperature.^{98,99} This may indicate controlled growth of polynuclear clusters/increase in the cluster size as the reaction temperature increases slowly. It is important to note that small copper selenide clusters form light-red, orange or purple crystals.⁷³ Keeping this in mind the initial attempts for the synthesis of copper selenide clusters which contain *bisNHC*^{Bn} was conducted by adding equimolar amount of $\text{Se}(\text{SiMe}_3)_2$ to a solution of $[(\text{CuCl})_2(\text{bisNHC}^{\text{Bn}})]$ (**2.4**) in DCM at -78°C . However, in this case, the reaction was apparently occurring in a fast manner resulting in an immediate color change from colorless to brownish black as the reaction solution warmed to -70°C . (colorless (-78°C) to light yellow (-76°C) to yellow (-74°C) to dark orange (-72°C) to brownish black (-70°C)). This might be resulting from the uncontrolled nucleation or aggregations of Cu_2Se subunits. As an attempt to get crystals, the brown reaction solution was layered with diethyl ether at -70°C and kept that undisturbed in an immersion cooler maintaining the temperature, resulting in an amorphous brown material and displayed a green luminescence. This solid was isolated, nevertheless it was found to be extremely temperature sensitive and decomposed at room temperature with solids becoming non-emissive. The same reactions were conducted in THF and THF:diethyl ether mixture (2.5:1) and the one in THF occurred in a relatively slow manner compared to that in DCM, however the solids formed after layering were still thermally sensitive.

The next logical step was an attempt to slow down the reaction by creating a competing environment for the copper centres to bind. This was done by adding a ligand with less σ -donating ability than NHC. Previous works from the Corrigan lab demonstrated the better stability of coinage metal chalcogenides stabilized by NHCs or CAACs compared to phosphine counterparts, primarily due to the greater σ -donating ability of the former.^{26,27} In this context, the weak σ donor PPh₃ was chosen so that the phosphine would not be expected to present in the final product bound to Cu, in turn retarding the apparent uncontrolled cluster growth.²⁶ The reaction was conducted by adding solution of PPh₃ dropwise to a solution of [(CuCl)₂(*bis*NHC^{Bn})] (**2.4**) while stirring at -30 °C in THF. The reaction proceeds from a light-yellow suspension to a clear light-yellow solution. The reaction solution was further cooled down to -78 °C followed by the addition of Se(SiMe₃) as outlined in **Scheme 2.4**.



Scheme 2.4: Reaction scheme for copper selenide with *bis*NHC^{Bn}.

Interestingly, no changes in solution properties were observed in the reaction solution until -30 °C. Storing the solution at -30 °C overnight resulted in the formation of brownish orange residue at the bottom of the Schlenk tube. The mother liquor was separated and the solvent was removed *in vacuo*, affording a white solid. The ³¹P{¹H} spectrum of the white solid in CDCl₃ shows three different chemical shifts corresponding to PPh₃ (-5.3 ppm), PPh₃O (29.1 ppm), and PPh₃Se (35.3

ppm). ^1H NMR spectrum of this solid indicated the absence of any $\text{bisNHC}^{\text{Bn}}$ ligand, confirming the selective binding of more σ -donating NHC ligands to copper centres.

The brownish orange solid was found to be sparingly soluble in common NMR solvents. The mass spectrum (ESI positive mode) indicates the presence of an interesting species at $m/z = 1099.33$ corresponding to $[\text{Cu}(\text{bisNHC}^{\text{Bn}})_2]^+$ (**Fig. 2.7**). This information is not entirely useful to confirm the copper selenide cluster formation as there were no signals from copper selenide fragments, even so it can be considered as evidence for the presence of $\text{bisNHC}^{\text{Bn}}$ bonded to the copper centres. There were peaks corresponding to $[(\text{bisNHC}^{\text{Bn}}) + \text{O} + \text{H}]^+$, $[\text{Cu}(\text{bisNHC}^{\text{Bn}})]^+$ similar to the mass spectrum of (**2.4**) suggesting the presence of starting material. The full mass spectrum is attached in the **Appendix** in *Figures S2.22*.

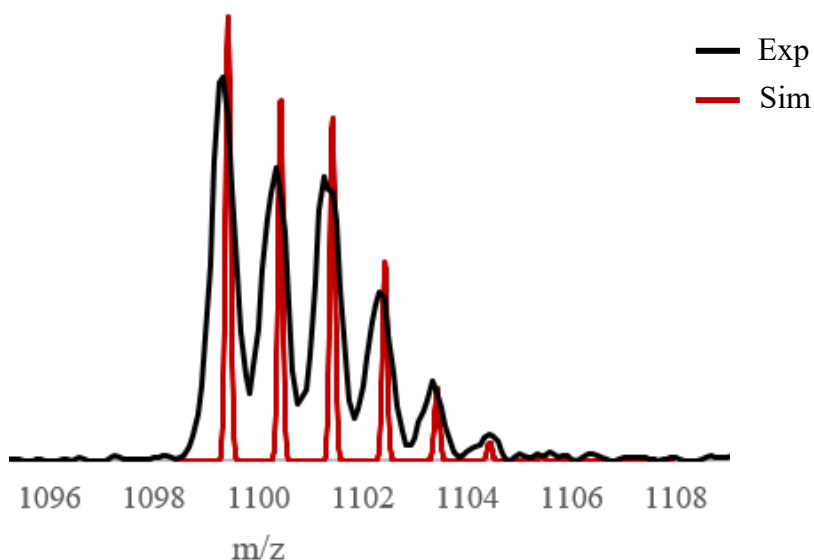


Figure 2.7: Experimental and simulated isotopic pattern for $[\text{Cu}(\text{bisNHC}^{\text{Bn}})_2]^+$ species ($m/z=1099.33$) observed in the mass spectrum of (**2.5**) in ESI positive mode.

2.2.2.2 Attempted synthesis of copper selenolates clusters with *bis*NHC^{Bn} (**2.6**)

Copper selenolates with *bis*NHC^{Bn} were targeted by adding 2.0 equivalents of PhSeSiMe₃ to a solution of [(CuCl)₂(*bis*NHC^{Bn})] (**2.4**) in THF at 0 °C. The reaction proceeds from a clear solution to the light-yellow reaction mixture with the formation of yellowish-white solids (**2.6**) after a day of stirring at RT. The mass spectroscopic studies of (**2.6**) revealed the limited fragmentation in both ESI positive and negative mode unlike (**2.3**). Poor solubility of (**2.6**) in common NMR solvents limit the characterization from NMR spectroscopy.

The X-ray photoelectron spectroscopic (XPS) analysis was performed on (**2.6**) to investigate the presence of copper and selenium. Initial XPS analysis displayed detectable copper signals. To investigate the elemental composition beyond surface, depth profiling was carried out by sputtering the sample with Ar⁺ ions. After sputtering (10 seconds), it only exhibits Cu2p signal, Cu 2p_{3/2} peak at 932.6 eV and a Cu 2p_{1/2} peak at 952.5 eV (**Fig 2.8**). These binding energies are consistent with copper in +1 oxidation state.¹⁰⁰ The signals from selenium were too weak and further high-resolution scans over extended time slightly enhanced the signal intensity for Se 3d. The Se 3d region showed a peak at around 54.6 eV. The oxidation state assignment was not performed on this Se 3d peak as the signal was broad and unresolved. Quantitative analysis yielded atomic percentages of 56.45% (Cu) and 43.55% (Se) suggesting a 1.3 to 1 ratio. After 30 second sputtering for depth profiling results 63.59% (Cu) and 36.41% (Se). A decline in the Se atomic percentage is possibly from sputtering-induced changes. Copper selenolates typically shows a 1:1 ratio between Cu(I) and PhSe⁻ and this deviation in these cases is likely from Se signals being weak or the sample might be undergoing degradation upon sputtering. Other signals found in the survey spectrum were from silicon grease. There was no signal for chlorine indicates that there is

no detectable starting material left. The full XPS survey spectrum is attached in **Appendix** in *Figure S2.17*.

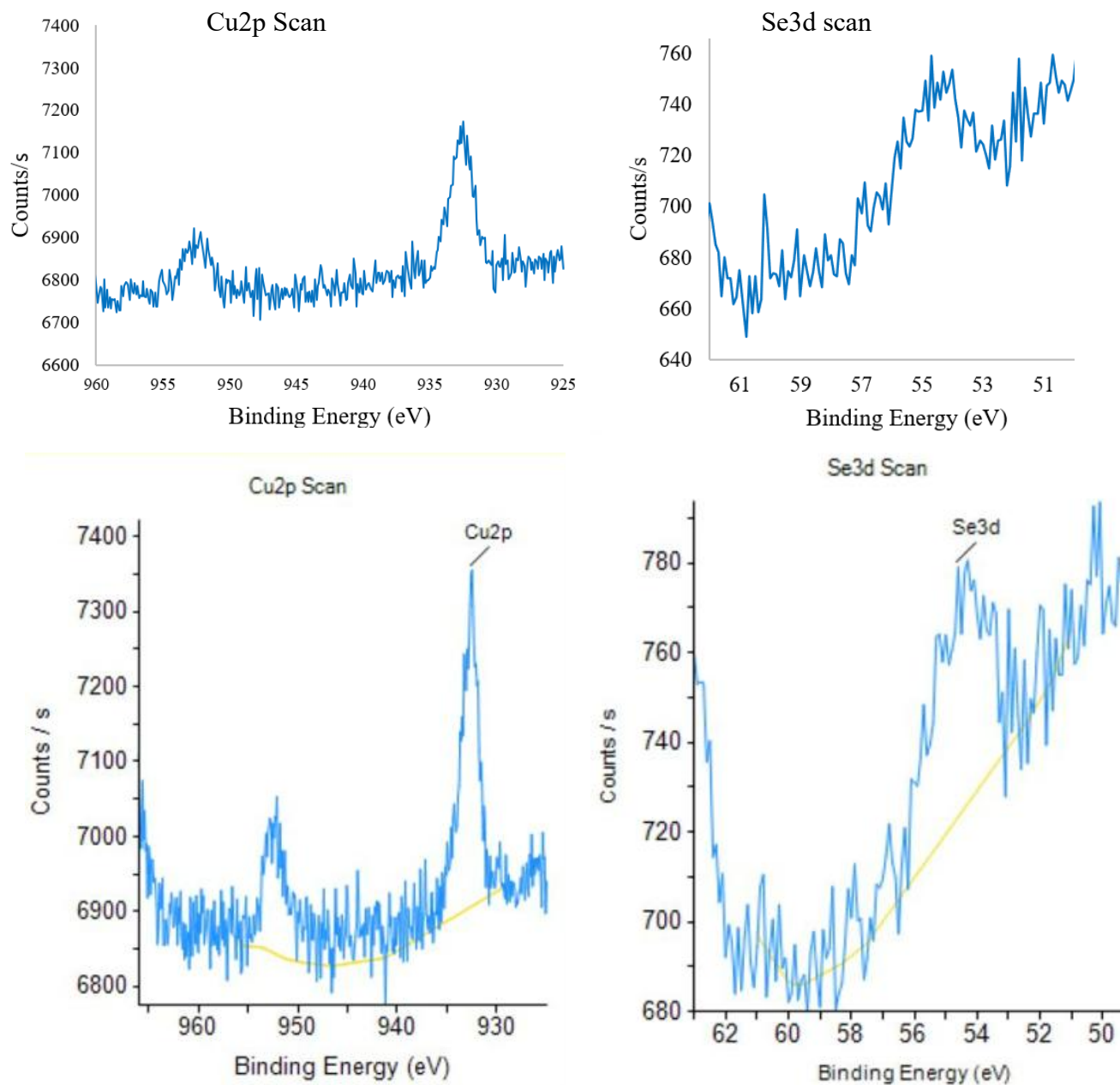


Figure 2.8: High resolution-XPS spectra of Cu 2p and Se 3d (top) after 10 second sputtering, (bottom) after 30 second sputtering.

The IR spectrum of **(2.6)** shows broad unresolved bands compared to that of $[(\text{CuCl})_2(\text{bisNHC}^{\text{Bn}})]$ **(2.4)**. The broad peaks in the range of $1253\text{--}771\text{ cm}^{-1}$ possibly from characteristic C-N stretches, C-H out of plane bending in NHC. The broad nature may result from the changes in the coordination environment with the introduction of selenolate. There is also a peak at around 3000 cm^{-1} suggesting aliphatic C-H stretch from the benzyl $-\text{CH}_2$ in NHC. The IR spectrum is attached in **Appendix** in *Figure S2.15*.

2.3 UV-vis absorption studies of **(2.1)**, **(2.2)**, **(2.3)**, **(2.4)**, **(2.5)**, **(2.6)**

Au(I) chalcogen compounds in particular show interesting photoluminescent properties due to the $d^{10}\text{--}d^{10}$ attraction strengthened by relativistic effects.²⁶ Benzimidazolium salt $[\text{bisNHC}^{\text{Bn}}\text{H}_2]\text{Cl}_2$ and $[(\text{AuOAc})_2(\text{bisNHC}^{\text{Bn}})]$ **(2.1)** were found to be non-emissive when irradiated with a handheld UV lamp ($\lambda = 254\text{ nm}$ and 365 nm). Interestingly, upon the addition of $\text{Se}(\text{SiMe}_3)_2$ and PhSeSiMe_3 , **(2.2)** and **(2.3)** exhibited intense red luminescence in solid state as given below.

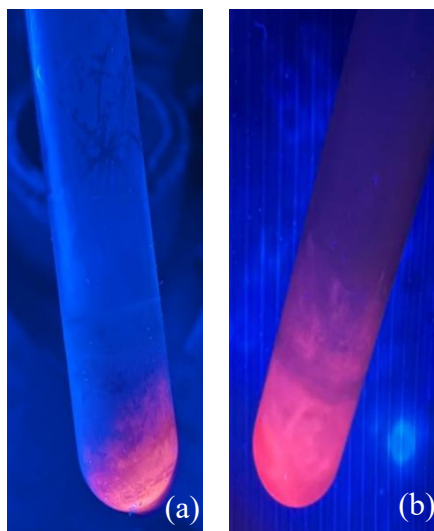


Figure 2.9: Solid state luminescence of (a) $[\text{Au}_6\text{Se}_2(\text{bisNHC}^{\text{Bn}})_3]^{2+}$ **(2.2)** and (b) $[(\text{AuSePh})_2(\text{bisNHC}^{\text{Bn}})]$ **(2.3)** at 77 K (irradiated with a UV lamp at 365 nm).

The luminescent behaviour of Cu(I) compounds was different than the Au(I) counter parts. For example, when copper(I) chloride was ligated to the *bis*NHC^{Bn} ligand, the resulting [(CuCl)₂(*bis*NHC^{Bn})] (**2.4**) exhibited green luminescence in the solid state at low temperature. The copper selenolate cluster which contain *bis*NHC^{Bn} (**2.6**) formed by the addition of PhSeSiMe₃, shows bright yellow luminescence when irradiated with the handheld UV lamp (**Fig. 2.10**). Copper selenide which contains *bis*NHC^{Bn} (**2.5**) shows yellowish-green luminescence in both solution and solid state.

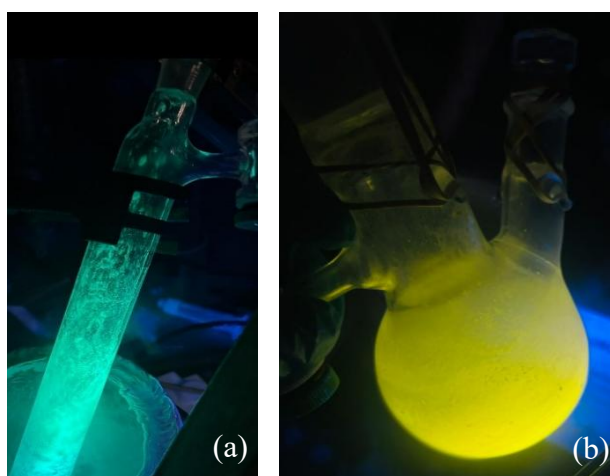


Figure 2.10: (a) Emission of (**2.4**) and (b) Emission of (**2.6**). (Qualitative observation of the emission of solid-state samples at 77 K when irradiated with handheld UV lamp at 365 nm).

The UV-vis absorption spectra were obtained for the benzimidazolium salt [*bis*NHC^{Bn}H₂]⁺Cl₂⁻, (**2.1**), (**2.2**), (**2.3**) in the solid state at room temperature. Benzimidazole based ligands typically exhibit absorption bands in the ultraviolet region of the UV-vis spectrum corresponding to π - π^* electronic transitions.⁵⁴ Therefore, the bands centred at 271 nm in the spectrum of

benzimidazolium salt is assigned to π - π^* transitions inside the benzimidazole moiety (**Fig 2.11**). The spectrum of **(2.1)** displayed a bathochromic shift of 16 nm with a λ_{max} at 287 nm. These bands are ascribed to the metal-perturbed ligand centered π - π^* transitions.⁵⁴ Interestingly, the absorption maximum in **(2.2)** is notably red shifted with a λ_{max} at 332 nm. This band may arise from metal-perturbed π - π^* transition with $\text{Se}^{2-} \rightarrow \text{Au}$ ligand-to-metal charge transfer (LMCT) character.¹⁰¹ This is type of ligand to metal charge transfer character is consistent with low energy LMCT excited states observed in selenium bridged group 11 metal compounds as reported by Villacampa *et al.*¹⁰¹ The shoulder peaks at around 377 nm and 489 nm are likely from cluster-enhanced LMCT ($\text{Se}^{2-} \rightarrow \text{Au}$) and contributions from metal centered $\text{Au } 5d \rightarrow \text{Au } 6sp$ transitions.¹⁰² The spectrum of **(2.3)** shows a peak at 295 nm suggesting the ligand centred π - π^* transitions.

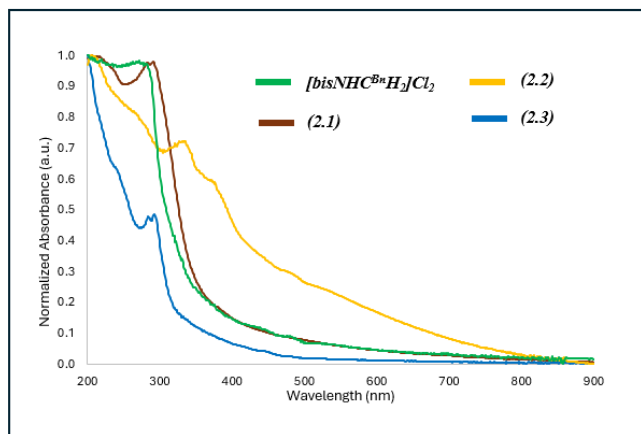


Figure 2.11: UV-vis Absorption spectra of $[\text{bisNHC}^{\text{Bn}}\text{H}_2]\text{Cl}_2$, $[(\text{AuOAc})_2(\text{bisNHC}^{\text{Bn}})]$ (**2.1**) $[\text{Au}_6\text{Se}_2(\text{bisNHC}^{\text{Bn}})_3]^{2+}$ (**2.2**) and $[(\text{AuSePh})_2(\text{bisNHC}^{\text{Bn}})]$ (**2.3**) (all spectra acquired by drop-casting the sample solution onto a quartz plate).

The UV-vis absorption of spectrum of $[(\text{CuCl})_2(\text{bisNHC}^{\text{Bn}})]$ (**2.4**) shows bands at 251 and 293 nm. The higher energy peak at 251 nm could be attributed to the ligand centered $\pi\text{-}\pi^*$ transitions, which is blue shifted relative to the $[\text{bisNHC}^{\text{Bn}}\text{H}_2]\text{Cl}_2$ (**Fig 2.12**). A peak 293 nm is likely from metal perturbed ligand centered transitions or metal to ligand charge transfer transitions suggesting metal-ligand interaction (Cu-NHC coordination). In the case of copper selenide with $\text{bisNHC}^{\text{Bn}}$ (**2.5**), it exhibits a peak at 244 nm (ligand centered $\pi\text{-}\pi^*$ transitions) and a new interesting (different than ligand centered $\pi\text{-}\pi^*$ transitions) red shifted broad absorption band at 326 nm, suggesting ligand to metal charge transfer transitions involving selenium. The shoulder peaks at 486 and 520 nm and a broad absorption band in the near infrared region are likely from cluster core transitions.⁶⁰ Copper selenolate with $\text{bisNHC}^{\text{Bn}}$ (**2.6**) shows a peak for ligand centered transitions (243 nm) and a peak similar to that in (**2.5**) at around 319 nm which is consistent with the incorporation of phenyl selenolate group suggesting the ligand to metal charge transfer transitions involving selenium.

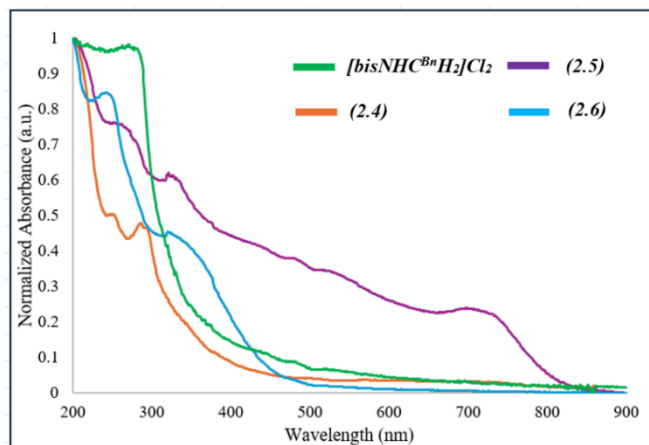


Figure 2.12: Uv-vis Absorption spectra of $[\text{bisNHC}^{\text{Bn}}\text{H}_2]\text{Cl}_2$, $[(\text{CuCl})_2(\text{bisNHC}^{\text{Bn}})]$ (**2.4**), copper selenides with $\text{bisNHC}^{\text{Bn}}$ (**2.5**), copper selenolates clusters with $\text{bisNHC}^{\text{Bn}}$ (**2.6**) (all spectra acquired by drop-casting the sample solution onto a quartz plate).

2.4 Conclusion

Au(I) chalcogen (E= Se) compounds stabilized by 1,1'-(dibenzyl)-3,3'-(1,2-xylylene)dibenzo[*d*]imidazol-2-ylidene) (*bis*NHC^{Bn}) were successfully synthesized. Gold acetate complex was found to be more reactive than chlorides towards silylated chalcogen reagents and resulted in the formation of [Au₆Se₂(*bis*NHC^{Bn})₃]²⁺ (**2.2**) and [(AuSePh)₂(*bis*NHC^{Bn})] (**2.3**). The mass spectrum of (**2.2**) however, indicated that there is more than one product in addition to a predominant peak corresponding to [Au₆Se₂(*bis*NHC^{Bn})₃]²⁺. The reactions of [(CuCl)₂(*bis*NHC^{Bn})] (**2.4**) with *bis*(trimethylsilyl)selenide were comparatively thermally sensitive and occurred in fast manner affecting the controlled cluster growth. The copper selenolate/selenide with *bis*NHC^{Bn} were attempted to synthesize and the complete characterization could not obtain considering the poor solubility of the isolated solids.

2.5 Experimental

2.5.1 General Considerations

All experiments were carried out under an inert atmosphere of high purity, dried nitrogen using standard Schlenk line techniques on a double manifold vacuum line. All solvents used were dried over molecular sieves (Type 3A) and stored under nitrogen.

Benzimidazole, benzyl bromide, 1,2-bis(chloromethyl)benzene were purchased from Sigma Aldrich and used without further purifications. Silver acetate was purchased from Fisher Chemicals and used without further purification. Copper (I) chloride purchased from Sigma Aldrich was purified by following the literature procedure.¹⁰³ Chloro(tetrahydrothiophene)gold(I) (Au(THT)Cl) was synthesised according to a literature procedure with few modifications.¹⁰⁴ *Bis*(trimethylsilyl)selenide and phenyl(trimethylsilyl)selenide were synthesized by a colleague using literature procedures and used without further purification.¹⁰⁵ 1,1'-(dibenzyl)-3,3'-(1,2-

xylylene)dibenzimidazolium dichloride [*bis*NHC^{Bn}H₂]₂Cl₂ was prepared by incorporating two literature procedures with few modifications.^{71,106}

¹H, ¹³C{¹H}, ³¹P{¹H} spectra were recorded on the Bruker Avance 300 with frequencies 300 MHz, 75 MHz, 121.5 respectively. The ¹H NMR spectra were referenced to residual proton solvent in CDCl₃ and DMSO-d₆. The ¹³C{¹H} NMR spectra were referenced to the carbon atoms in CDCl₃ and DMSO-d₆. Low-resolution mass spectra of samples **(2.1)**, **(2.2)**, **(2.3)**, **(2.4)**, **(2.5)** were obtained via electrospray ionization (ESI), which was measured on a Thermo LTQ-XL instrument. Envipat (<https://www.envipat.eawag.ch/index.php>) software was used for calculating isotope patterns. Total Reflectance Infrared (ATR-IR) spectra of samples [*bis*NHC^{Bn}H₂]₂Cl₂, **(2.1)**, **(2.2)**, **(2.3)**, **(2.4)**, **(2.5)**, **(2.6)** were obtained using Bruker Tensor 27 Spectrometer. UV-vis absorption spectrum of [*bis*NHC^{Bn}H₂]₂Cl₂, **(2.1)**, **(2.2)**, **(2.3)**, **(2.4)**, **(2.5)**, **(2.6)** were recorded on a PerkinElmer Lambda 1050 spectrometer at the University of Waterloo WATLab facility. X-ray photoelectron spectra of sample **(2.6)** were recorded on Nexsa G2 surface analysis system, Thermo Scientific (X-ray source: Monochromatic Al K-alpha). Melting point measurements were carried out on a Digimelt apparatus under nitrogen gas.

2.5.2 Synthesis of [(AuOAc)₂(*bis*NHC^{Bn})] (**2.1**)

To prepare [(AuCl)₂(*bis*NHC^{Bn})], a mixture of 1,1'-(dibenzyl)-3,3'-(1,2-xylylene)dibenzimidazolium dichloride [*bis*NHC^{Bn}H₂]₂Cl₂ (0.115 g, 0.196 mmol, 1 equiv.) and chloro(tetrahydrothiophene)gold(I) (Au(THT)Cl) (0.126 g, 0.393 mmol, 2 equiv.) dissolved in 20 mL of ACN. Triethylamine (Et₃N) (0.060 mL, 0.420 mmol, 2.2 equiv.) was added and the mixture was refluxed for 3 h.¹⁰⁷ After 3 h, more Et₃N was added, and refluxing was continued for 30 min. ACN was removed *in vacuo* and the resulting purplish white solid was thoroughly washed with water (10 mL × 3), filtered off, washed with diethyl ether (8 mL × 1) and dried for 2-3 hr to afford

the crude residue. The resulting solid was then dissolved in dichloromethane (DCM), filtered over silica gel (20:1 DCM/MeOH eluent) and the volatiles were removed in *in vacuo* affording the pure complex as a white powder. AgOAc (0.075 g, 0.450 mmol, 2.6 equiv.) was added to a solution of $[(\text{AuCl})_2(\text{bisNHC}^{\text{Bn}})]$ (0.170 g, 0.173 mmol, 1.0 equiv.) alongside 15 mL of DCM and stirred for 4 h in the absence of light.⁹³ The reaction mixture was filtered over Celite, and volatiles were removed *in vacuo* affording complex **(2.1)** as a white powder. Yield = 99 %. ^1H NMR (300 MHz; CDCl_3): δ 7.62-7.60 (m, 2H), , 7.42 (m, 4H), 7.39 (m, 4H), 7.37 (m, 4H), 7.33 (m, 2H), 7.31 (m, 2H), 7.18-7.15 (m, 2H), 6.76-6.73 (m, 2H), 6.07 (s, 4H), 5.78 (s, 4H), 2.00 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ (75 MHz; CDCl_3): δ 177.31, 174.03, 134.64, 134.17, 133.13, 132.75, 129.20, 128.71, 127.60, 126.79, 125.32, 124.96, 112.76, 112.20, 53.24, 49.92, 23.98. **LR-ESI-MS (m/z)** for $[\text{C}_{38}\text{H}_{33}\text{N}_4\text{O}_2\text{Au}_2]^+$: calculated 971.19, found 970.55. ATR-FTIR (cm^{-1}): 1606.48, m.p= 175.2-178.5 °C_{decomp}. Elemental analysis: TBD. ^1H , $^{13}\text{C}\{^1\text{H}\}$ NMR, IR, and mass spectra are attached in the **Appendix** in *Figures S2.4, S2.5, S2.10 and S2.18*.

2.5.3 Synthesis of $[\text{Au}_6\text{Se}_2(\text{bisNHC}^{\text{Bn}})_3]^{2+} (\text{OAc})_2$ (**2.2**) (OAc)₂

Compound **(2.1)** (0.073 g, 0.071 mmol, 1 equiv.) was dissolved in THF and stirred for 15 minutes. *Bis*(trimethylsilyl)selenide (0.017 mL, 0.017 mmol, 1.0 equiv.) was added while stirring at -78 °C. The solution was warmed slowly to -30 °C resulting in a clear and colorless solution. It was then moved to freezer (-30 °C). There were no crystals or solids after two days and the clear solution was layered with ether. After a day, off-white solids were observed. The resulting solid was isolated and washed with 15 mL of hexane and dried in *in vacuo* for 2-3 hours. Yield = 60 %. **ESI-MS (m/z)** for $[\text{Au}_6\text{Se}_2(\text{bisNHC}^{\text{Bn}})_3]^{2+}$: calculated = 1448.18, found = 1448.25. m.p= 216 °C_{decomp}. FT-IR and mass spectrum is attached in the **Appendix** in *Figure S2.11 and S2.19*. Elemental analysis: To be determined.

2.5.4 Synthesis of [(AuSePh)₂(bisNHC^{Bn})] (2.3)

Compound **(2.1)** (0.073 g, 0.071 mmol, 1 equiv.) was dissolved in 10 mL THF and stirred for 30 minutes. Phenyl(trimethylsilyl)selenide (0.027 mL, 0.142 mmol, 2 equiv.) was added while stirring at 0 °C. The solution was warmed slowly to room temperature and stirred overnight. The titled product was precipitated from heptane yielding a yellow solid. Yield = 55 %. ¹H NMR (300 MHz; CDCl₃): δ 7.60 (m, 4H), 7.52-7.38 (m, 14 H), 7.36-7.32 (m, 10 H), 6.90-6.78 (m, 4H), 5.99 (s, 4H), 5.79 (s, 4H). LR-ESI-MS (*m/z*) for [Au₂(SePh)(bisNHC^{Bn})]⁺: calculated 1069.14, found 1069.16. m.p= 232.5 °C_{decomp}. ¹H NMR, IR and mass spectrum are attached in the **Appendix** in *Figures S2.6, S2.12, S2.20*. Elemental analysis: To be determined.

2.5.5 Synthesis of [(CuCl)₂(bisNHC^{Bn})] (2.4)

A mixture of 1,1'-(dibenzyl)-3,3'-(1,2-xylylene)dibenzimidazolium dichloride [bisNHC^{Bn}H₂]⁺Cl₂ (1.0 g, 1.694 mmol, 1 equiv.) and copper (I) chloride (0.335 g, 3.338 mmol, 2 equiv.) was dissolved in 25 mL of ACN, triethylamine (Et₃N) (0.56 mL, 3.988 mmol, 2.3 equiv.) was added, and the mixture was refluxed for 3 h.¹⁰⁷ After 3 h, more Et₃N (0.56 mL, 3.988 mmol, 2.3 equiv.) was added, and refluxing was continued for 30 min. ACN was removed *in vacuo* and the resulting yellow solid was thoroughly washed ACN (20 mL x 2) followed by washing with water (10 mL × 3), filtered off, washed with 1:3 MeOH-ether mixture for several times (8 mL × 1) and dried for 2-3 hr to afford the complex **(2.4)**. Yield = 60%. ¹H NMR (300 MHz; DMSO-*d*₆): δ 7.75-7.72 (m, 2H), 7.68-7.65 (m, 2H), 7.44 (m, 2H), 7.41 (m, 2H), 7.37-7.34 (m, 4H), 7.33-7.28 (m, 6H), 7.26-7.24 (m, 2H), 7.03-7.00 (m, 2H), 5.96 (s, 4H), 5.73 (s, 4H). ¹³C {¹H} NMR (75 MHz; DMSO- *d*₆): δ 186.88, 136.40, 134.57, 133.81, 133.12, 129.08, 128.79, 128.57, 128.39, 128.21, 128.03, 127.55, 127.33, 124.00, 51.47, 48.52. m.p= > 260 °C_{decomp}. ESI-MS (*m/z*) for [(CuCl)(bisNHC^{Bn}) + H]⁺:

calculated = 617.14, found = 617.16. ^1H , $^{13}\text{C}\{^1\text{H}\}$ NMR, IR and mass spectrum are attached in the **Appendix** in *Figures S2.7, S2.8, S2.13 and S2.21*.

2.5.6 Attempted synthesis of copper selenide with bisNHC^{Bn} (2.5)

Compound (**2.4**) (0.050 g, 0.069 mmol, 1 equiv.) was dissolved in 30 mL of THF and sonicated for 30 min. PPh_3 (0.036 g, 0.139 mmol, 2 equiv.) in THF was added dropwise while stirring at $-30\text{ }^\circ\text{C}$. *Bis*(trimethylsilyl)selenide (0.017 mL, 0.069 mmol, 1.0 equiv.) was added to the resulting clear light-yellow solution while stirring at $-78\text{ }^\circ\text{C}$. The reaction solution was slowly warmed to $-30\text{ }^\circ\text{C}$ and stored at $-30\text{ }^\circ\text{C}$ overnight forming a brown solution with a brownish orange residue at the bottom of the schlenk tube. This solid was isolated and washed with 10 mL ether, dried *in vacuo*. Yield = 54 %. m.p = $186.3\text{ }^\circ\text{C}_{\text{decomp}}$. IR and mass spectrum is attached in the **Appendix** in *Figure S2.14 and S2.22*.

2.5.7 Attempted synthesis of copper selenolate with bisNHC^{Bn} (2.6)

Compound (**2.3**) (0.118 g, 0.165 mmol, 1 equiv.) was dissolved in 10 mL THF and stirred for 30 minutes. Phenyl(trimethylsilyl)selenide (0.064 mL, 0.329 mmol, 2 equiv.) was added while stirring at $0\text{ }^\circ\text{C}$. The solution was warmed slowly to room temperature and stirred overnight resulting a yellowish white amorphous material. Removed the solvent and dried *in vacuo*. Yield = 46 %. m.p. = $229.5\text{ }^\circ\text{C}_{\text{decomp}}$. IR spectrum and XPS survey is attached in the **Appendix** in *Figure S2.15 and S2.17*.

2.6 Percent buried volume ($\%V_{bur}$) of $bisNHC^{Bn}$

$\%V_{bur}$ of $bisNHC^{Bn}$ ligand is calculated using SambVca 2.1 web tool.⁴⁵ The crystallographic data is used from the literature.⁹³ The Au-NHC distance has been fixed at 2 Å. The X and Y axis correspond to the cartesian coordinates (in Å) in the plane perpendicular to the metal-ligand bond axis. The steric map obtained is displayed below. The steric impact of this bulky ligand was found be 59.2 %.

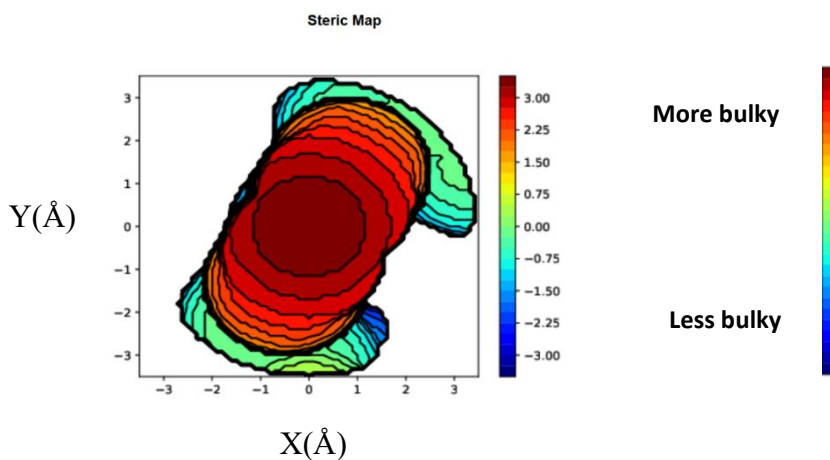


Figure 2.13: Steric profile of $bisNHC^{Bn}$ around the metal centre.

Chapter 3

3.0 Summary and future research directions

3.1 Summary and Conclusions

The work in this thesis describes the synthesis and characterization of gold chalcogen clusters and attempted synthesis of copper chalcogen clusters with a rigid bidentate N-heterocyclic carbene ligand.

Gold(I) chalcogenide clusters are synthesized by preparing a new precursor $[(\text{AuOAc})_2(\text{bisNHC}^{\text{Bn}})]$ (**2.1**). This complex was mainly characterized by NMR spectroscopy and mass spectrometric methods. **2.1** was subsequently reacted with silylated selenium reagents to target $[\text{Au}_6\text{Se}_2(\text{bisNHC}^{\text{Bn}})_3]^{2+}$ (**2.2**) and $[(\text{AuSePh})_2(\text{bisNHC}^{\text{Bn}})]$ (**2.3**). (**2.2**) was partially characterized with the aid of mass spectrometry. The mass spectrum of (**2.2**) indicated that there is more than one product however, the predominant peak corresponds to the $[\text{Au}_6\text{Se}_2(\text{bisNHC}^{\text{Bn}})_3]^{2+}$ dication. Based on the limited characterization data of the gold selenide cluster, it is impossible to confirm the structural parameters for $[\text{Au}_6\text{Se}_2(\text{bisNHC}^{\text{Bn}})_3]^{2+}$ or indeed the make up of other products in the reaction mixture. NMR characterization of (**2.2**) could not be obtained considering the limited solubility of reaction mixtures in common NMR solvents. In the case of (**2.3**) the mass spectroscopic results show only one peak suggesting the successful formation of $[(\text{AuSePh})_2(\text{bisNHC}^{\text{Bn}})]$. At the same time, the limited solubility of (**2.3**) in common solvents is unexpected. The initial attempts to target gold (I) selenium clusters starting from the $[(\text{AuCl})_2(\text{bisNHC}^{\text{Bn}})]$ complex were found to be even less selective and reactions involving (**2.1**) were more suitable via the displacement of coordinated OAc and reaction completion.

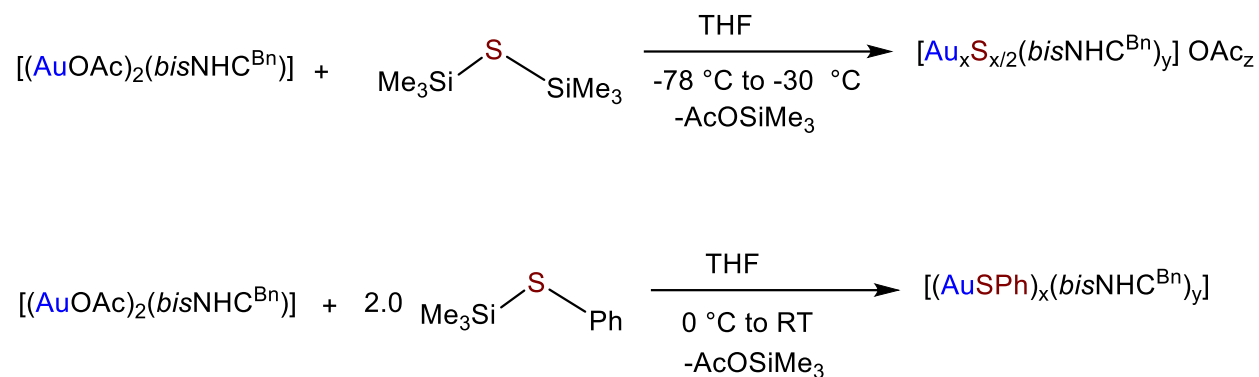
Copper selenide/chalcogenolate clusters with $bisNHC^{Bn}$ were targeted from the complex $[(CuCl)_2(bisNHC^{Bn})]$ (**2.4**). It was mainly characterized by NMR spectroscopy. In contrast to the Au(I) analogues, the solids obtained from the reactions of $Se(SiMe_3)_2$ with $[(CuCl)_2(bisNHC^{Bn})]$ (**2.4**), were difficult to characterize due to the poor solubility and poor thermal stability. As an attempt to control the uncontrolled cluster growth, a weak σ donor PPh_3 was added to a solution of (**2.4**) before introducing $Se(SiMe_3)_2$. This resulted in comparatively slower reaction (based on the color changes upon warming up to $-30\text{ }^\circ\text{C}$). Efforts to characterize the solid with the aid of mass spectrometry were unsuccessful and there were no indications of copper selenide cluster fragments.

The synthesis of copper selenolates with $bisNHC^{Bn}$ were attempted and the isolated solid shows limited fragmentation in both ESI positive and negative mode. It lacks solubility in common NMR solvents. Therefore, X-ray photoelectron analysis was performed and detectable copper and selenium signals were found. In contrast to Au(I) analogues, the preparation and characterization of Cu(I) selenide and selenolate (solution state studies in particular) with $bisNHC^{Bn}$ were found to be more challenging.

3.2 Future research directions

3.2.1 Au(I) chalcogen compounds with $bisNHC^{Bn}$

Future work in this field of Au(I) chalcogen chemistry should include incorporation of the chalcogen S. The aim is to synthesize sulfur analogues of (2.2) and 2.3) by adding $S(SiMe_3)_2$ or $PhSSiMe_3$ to a solution of $[(AuOAc)_2(bisNHC^{Bn})]$, respectively. (**Scheme 3.1**)



Scheme 3.1: Proposed synthetic scheme for metal chalcogenide/chalcogenolate clusters employing S(SiMe₃)₂ and PhSSiMe₃.

Repeated attempts to obtain crystals of **(2.2)**, **(2.3)** and gold selenides formed from chloride starting material - [(AuCl)₂(bisNHC^{Bn})] were forming either amorphous materials or microcrystals not suitable for single crystal X-ray studies.

3.2.2 Cu(I) chalcogen compounds with bisNHC^{Bn}

Future work in this vein of research would include the reactions involving [(CuX)₂(bisNHC^{Bn})] (X= Cl, OAc) with S(SiMe₃)₂. The aim is to form smaller assemblies of copper sulfide units and to explore possibilities of obtaining single crystals.

3.2.3 Ligand modification

The poor solubility of associated with gold(I) selenides, copper (I) selenolates/selenides can be improved by introducing different linkers such as alkyl groups (n= 1, 2, 3) in the bidentate NHC (**Fig 3.1**). The aim is to improve the solubility in common NMR solvents such as CDCl₃. Improving the solubility will aid in exploring the solution state absorption/emission studies and helps in obtaining suitable single crystals.

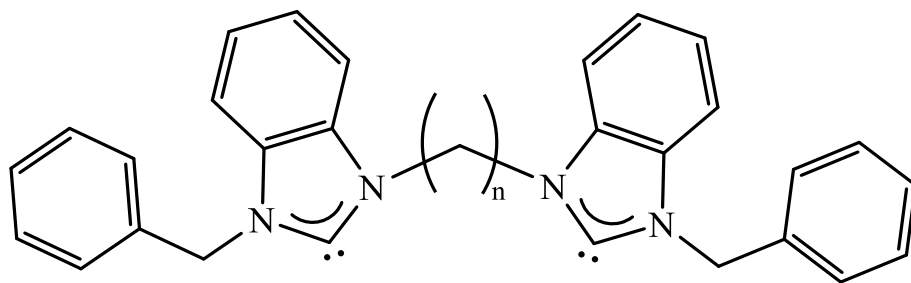


Figure 3.1: Ligand modification in bidentate NHC.

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Publication: European Journal of Inorganic Chemistry

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Publication: Journal of the American Chemical Society

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Author: Emily L. Albright, Tetyana I. Levchenko, Viveka K. Kulkarni, et al

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Appendices

Appendix 2.0 Supporting Information for Chapter 2

Appendix 2.1: NMR spectra

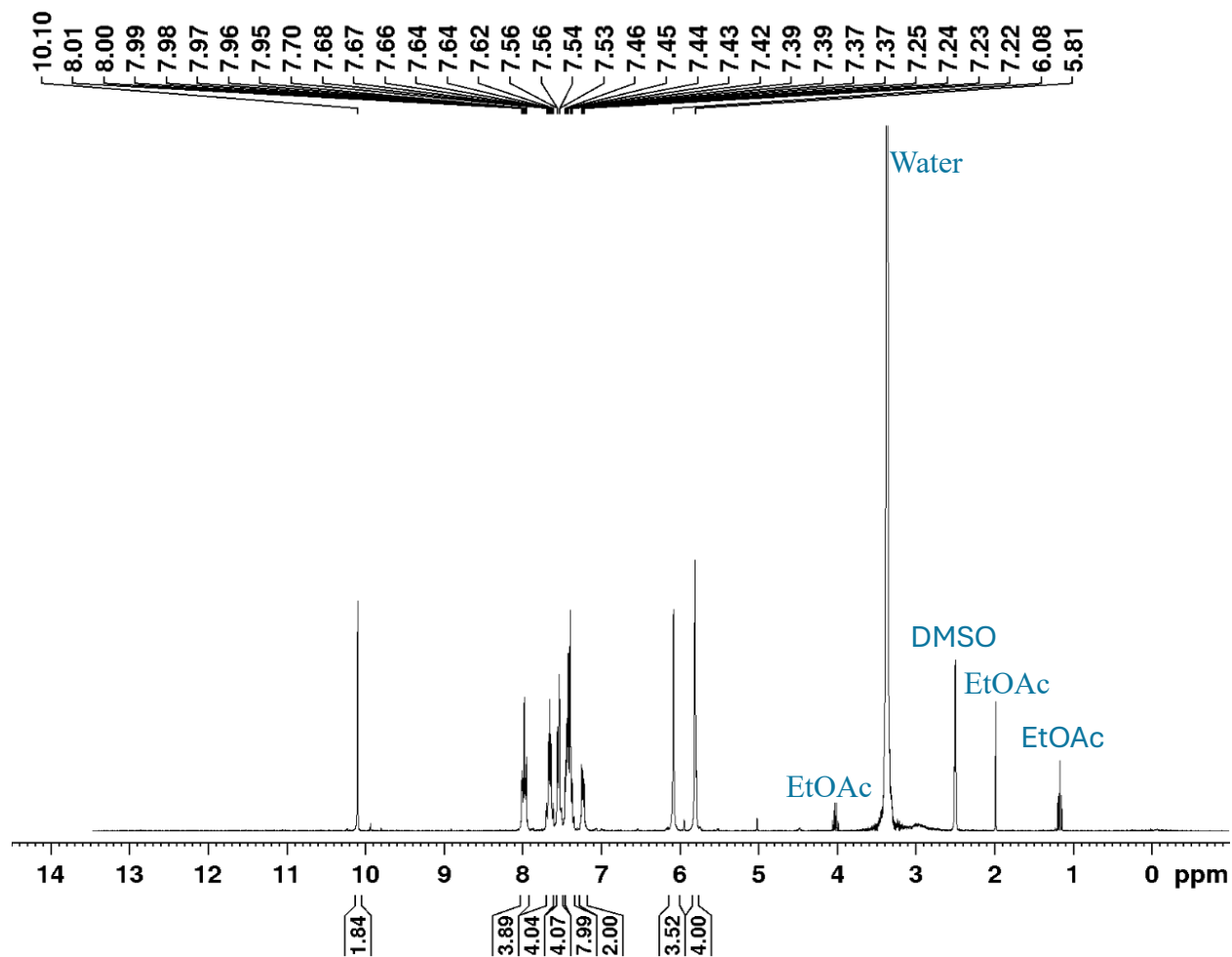


Figure S2.1: ^1H NMR spectrum of $[\text{bisNHC}^{\text{Bn}}\text{H}_2]\text{Cl}_2$ in $\text{DMSO}-d_6$.

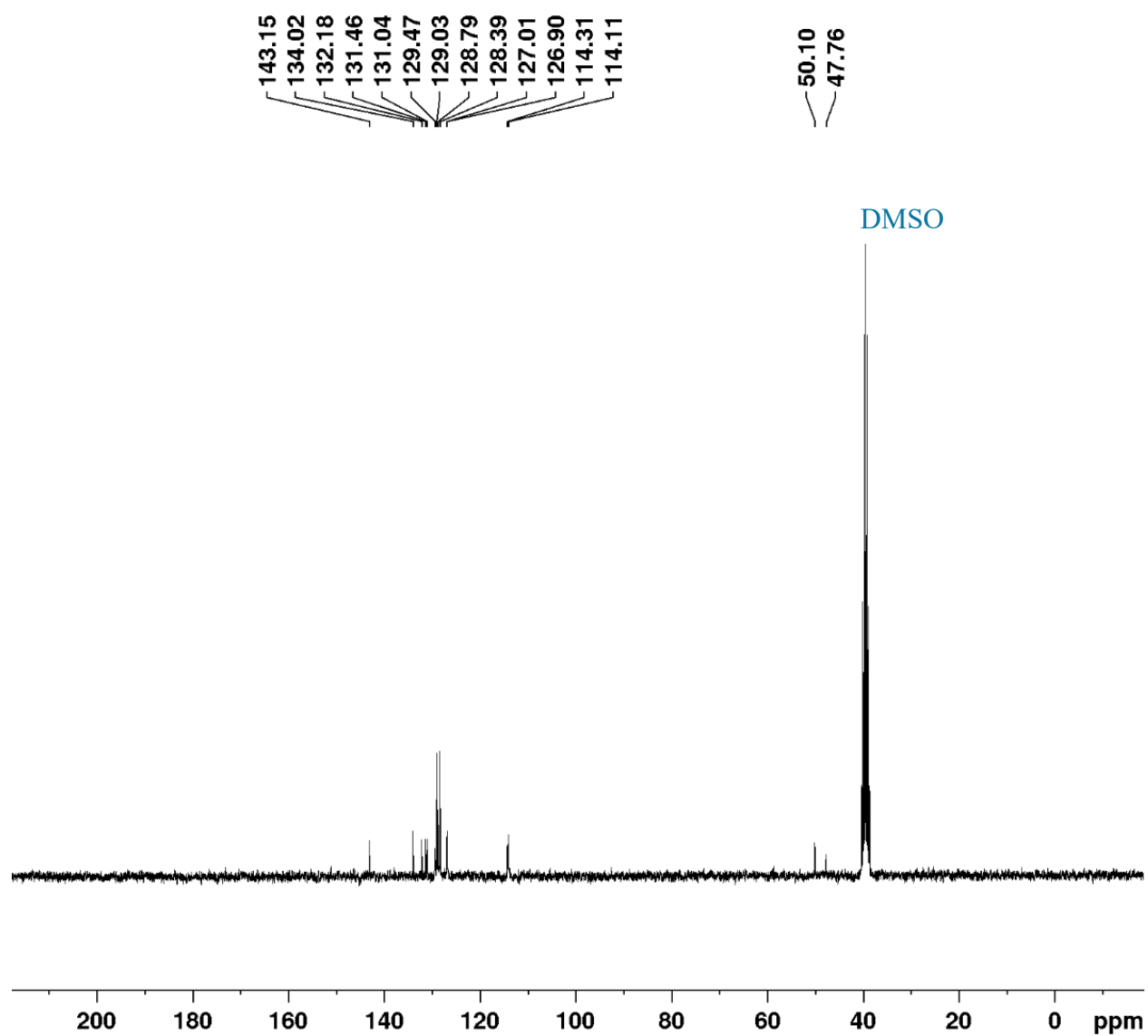


Figure S2.2: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\text{bisNHC}^{\text{Bn}}\text{H}_2]\text{Cl}_2$ in $\text{DMSO-}d_6$.

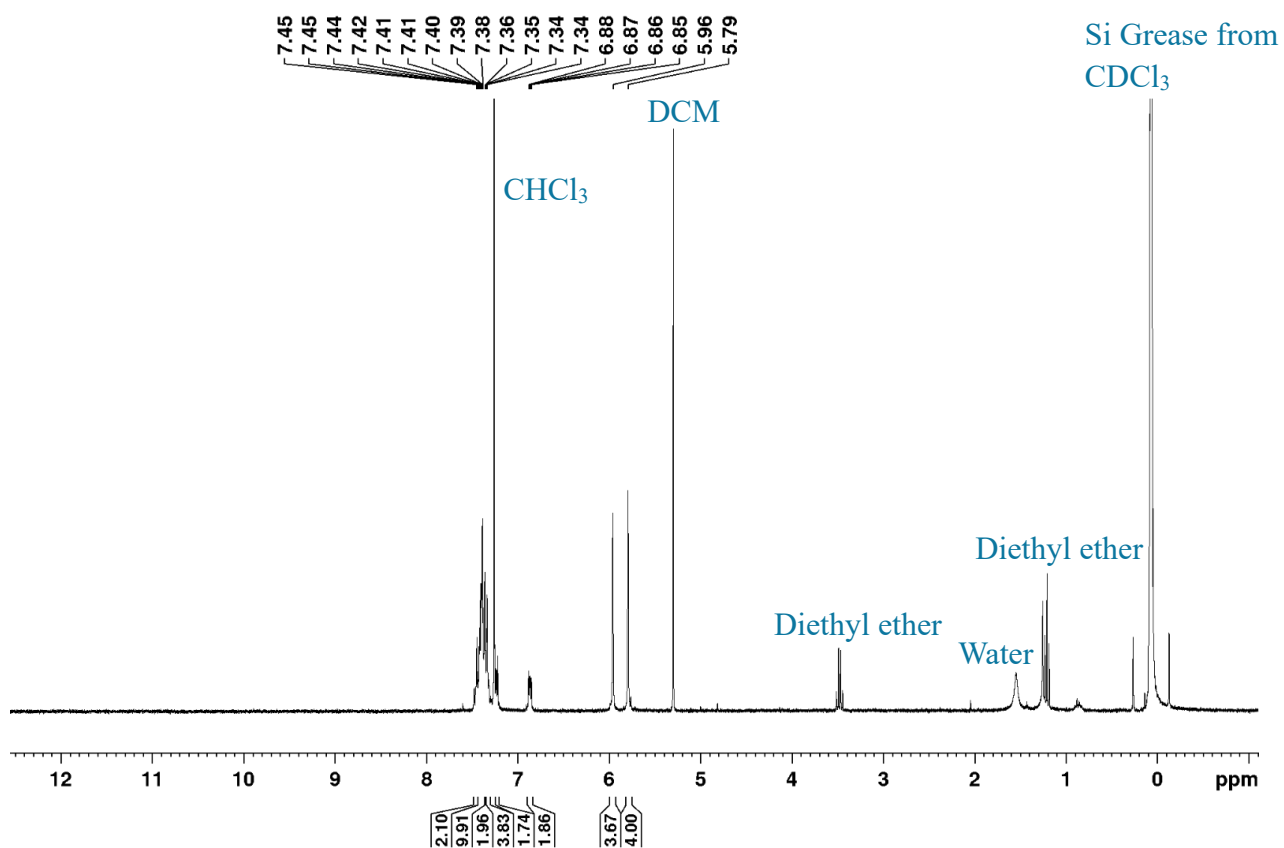


Figure S2.3: ^1H NMR spectrum of $[(AuCl)_2(bisNHC^{Bn})]$ in $CDCl_3$.

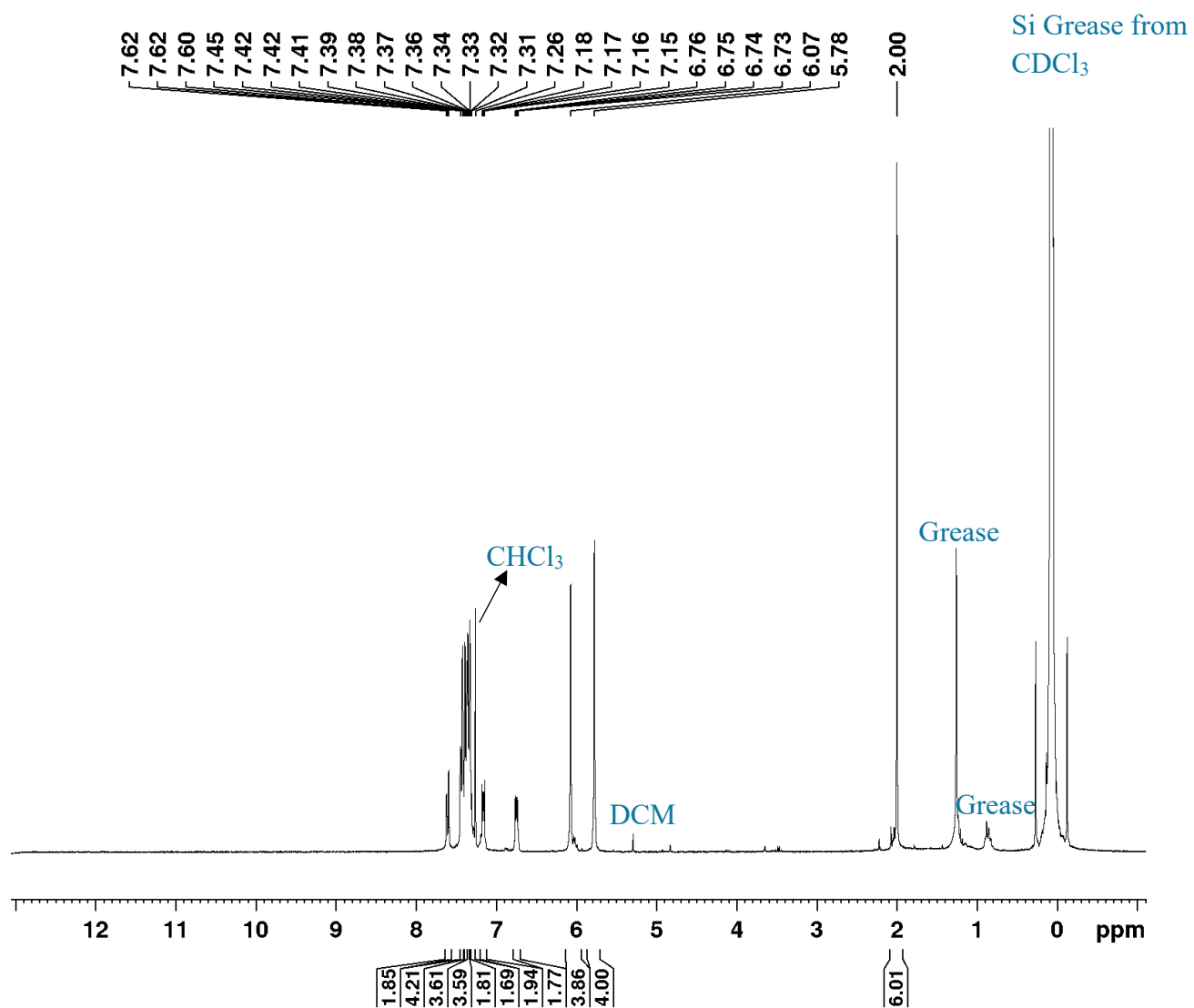


Figure S2.4: ^1H NMR spectrum of $[(\text{AuOAc})_2(\text{bisNHC}^{\text{Bn}})]$ (**2.1**) in CDCl_3 .

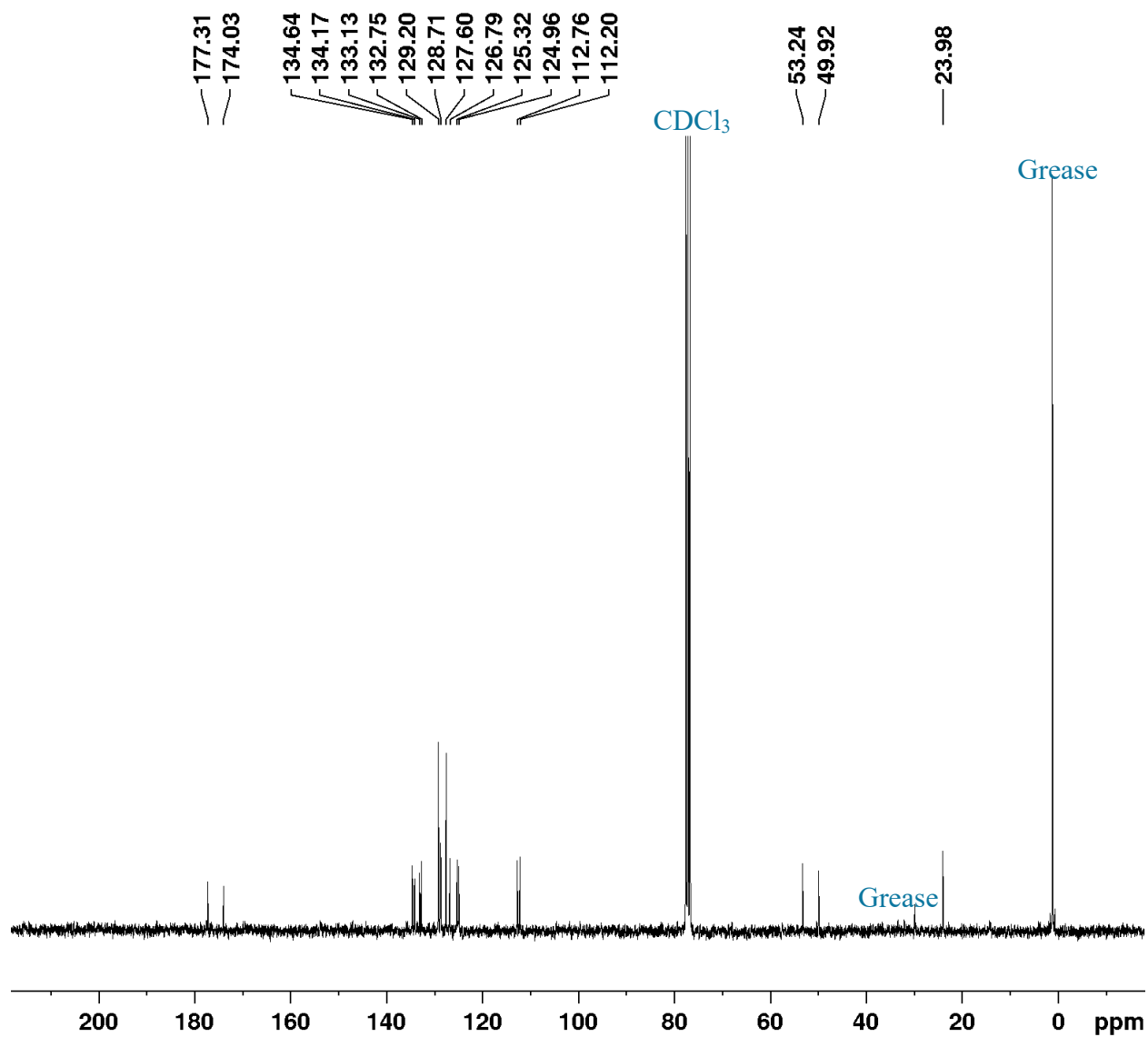


Figure S2.5: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[(\text{AuOAc})_2(\text{bisNHC}^{\text{Bn}})]$ (**2.1**) in CDCl_3

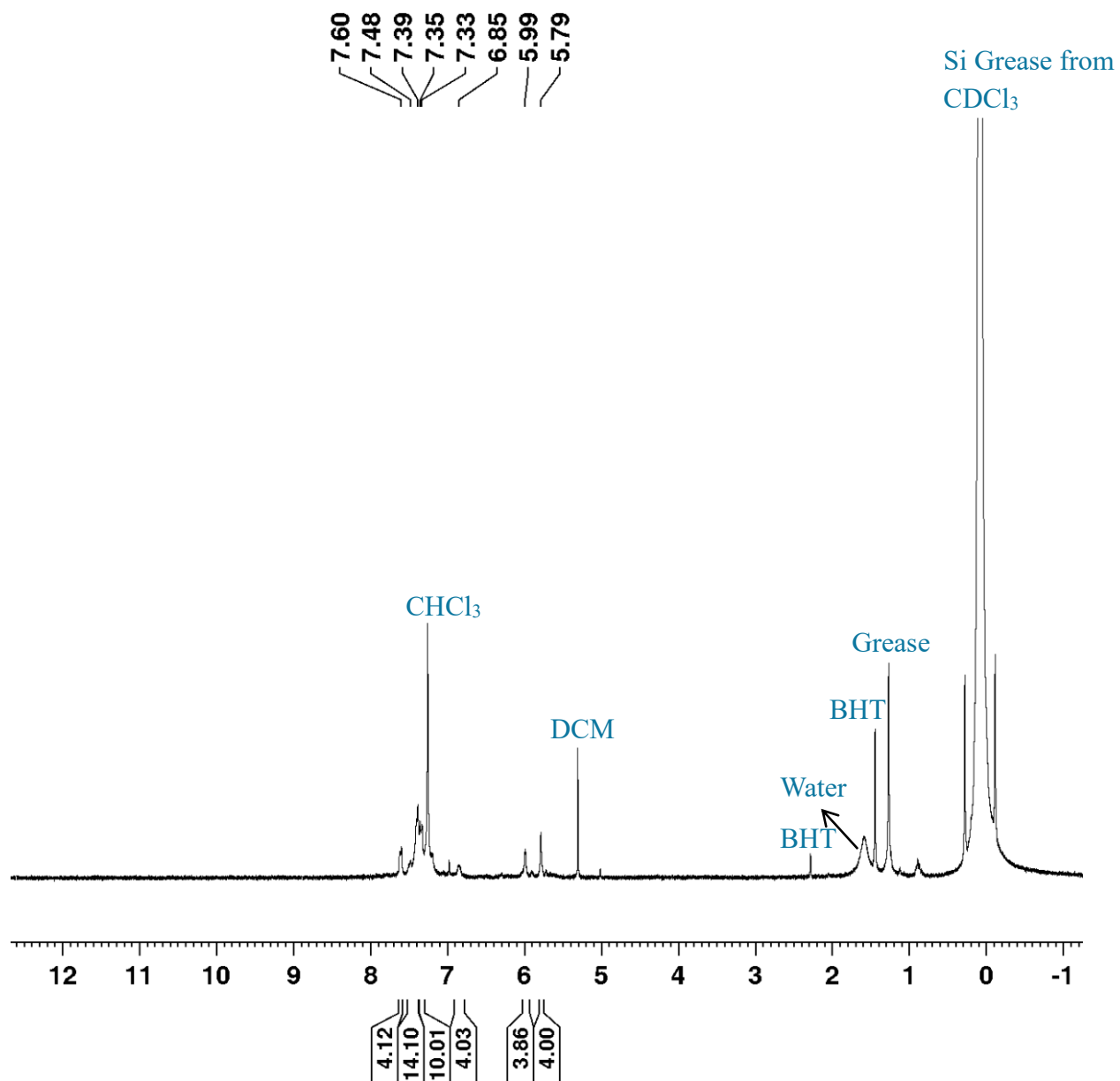


Figure S2.6: ¹H NMR spectrum of $[(\text{AuSePh})_2(\text{bisNHC}^{\text{Bn}})]$ (**2.3**) in CDCl_3 .

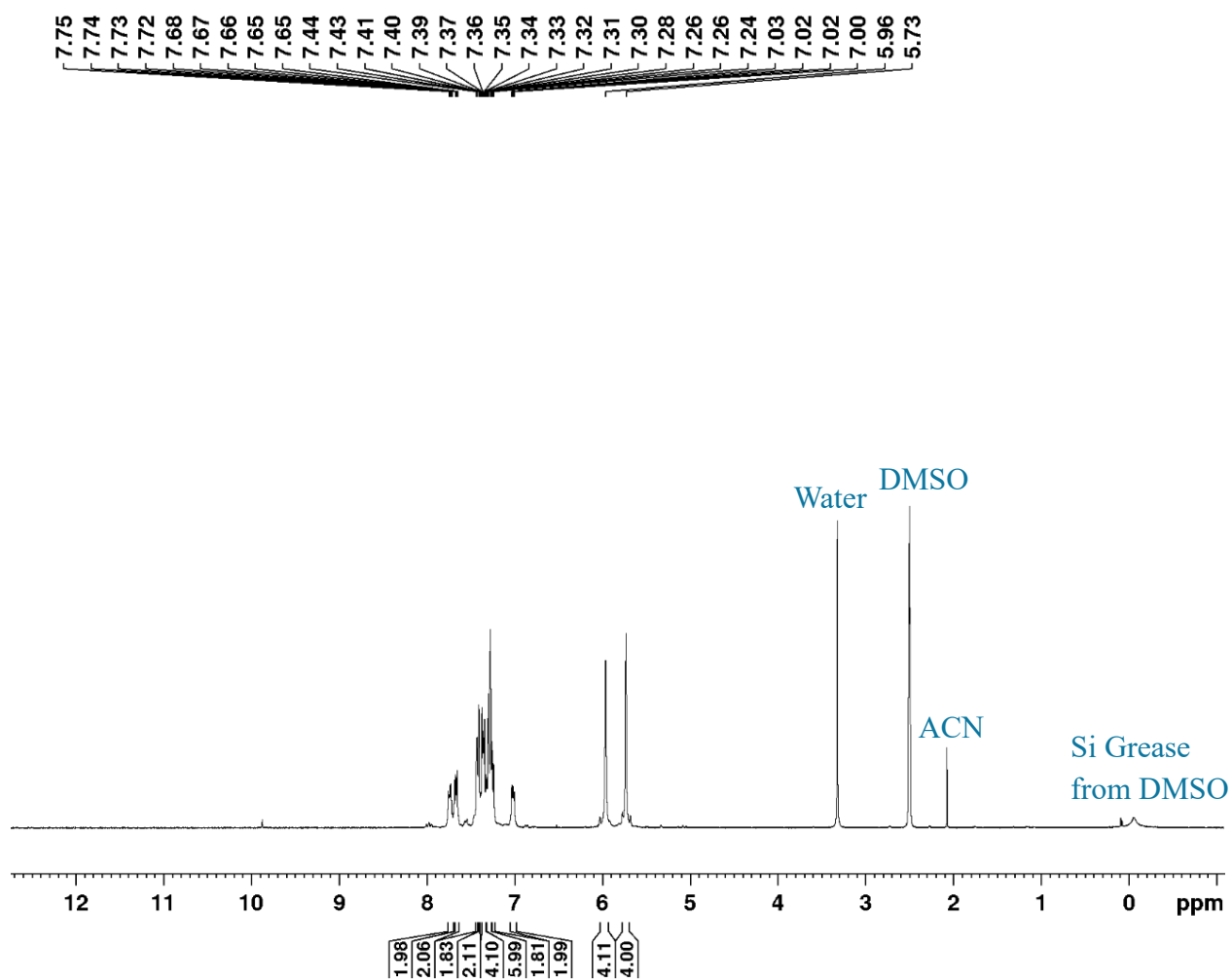


Figure S2.7: ^1H NMR spectrum of $[(\text{CuCl})_2(\text{bisNHC}^{\text{Bn}})]$ (**2.4**) in $\text{DMSO-}d_6$.

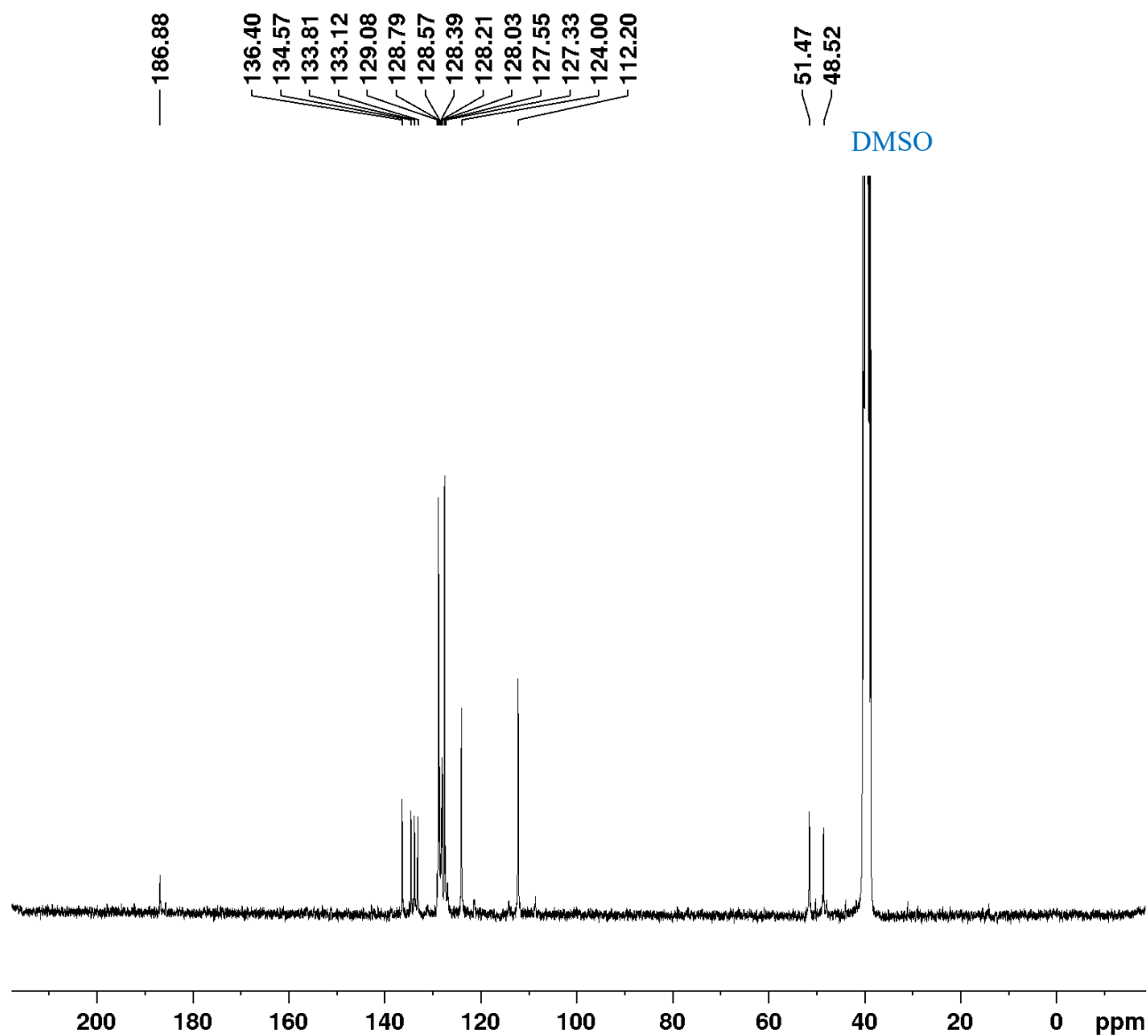


Figure S2.8: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[(\text{CuCl})_2(\text{bisNHC}^{\text{Bn}})]$ (2.4) in $\text{DMSO-}d_6$.

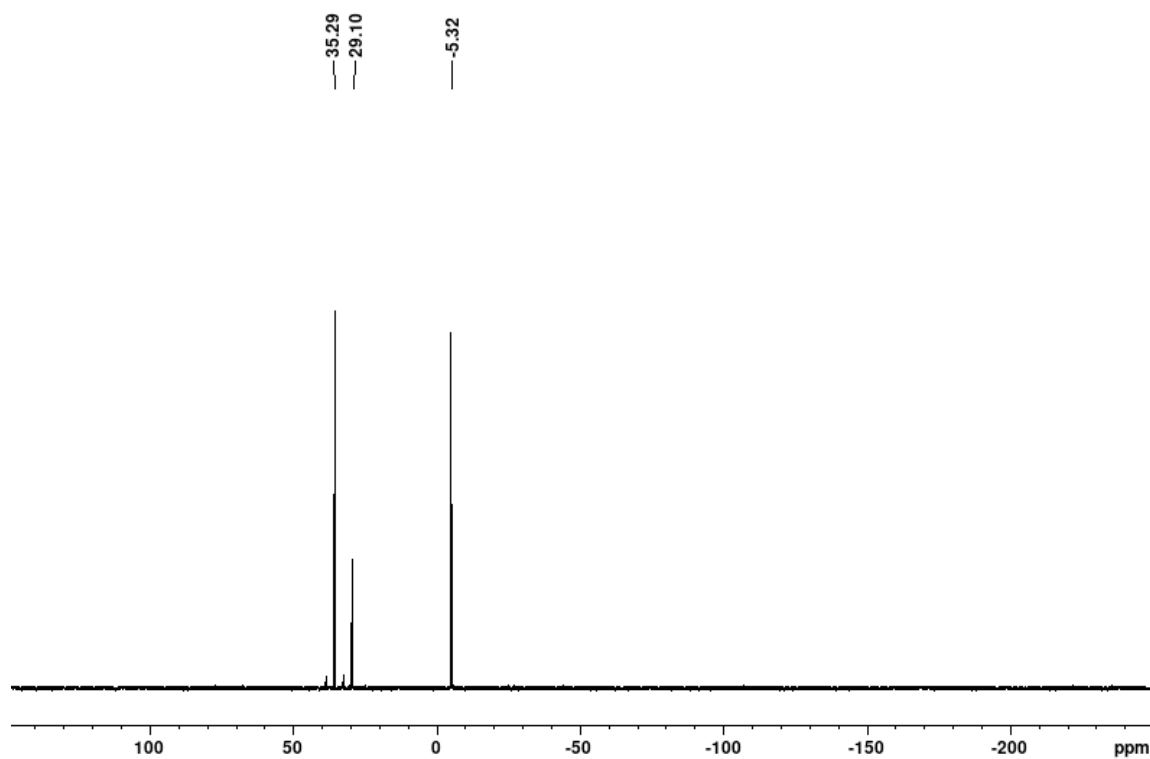


Figure S2.9: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the white solid obtained from the mother liquor of copper selenide reaction mixture in CDCl_3 .

Appendix 1.2: FTIR spectra

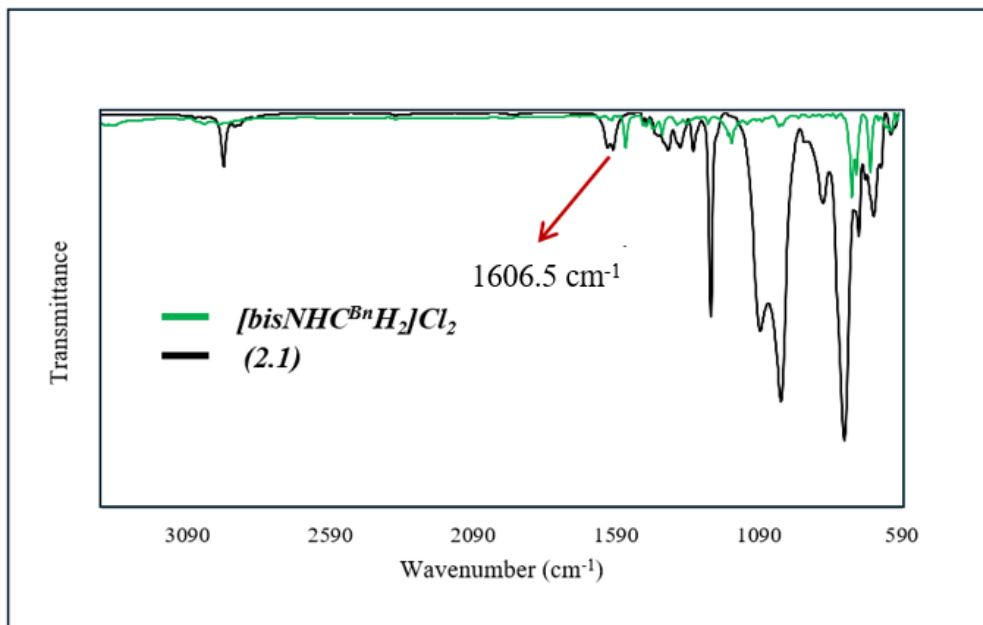


Figure S2.10: FT-IR spectrum of $[bisNHC^{Bn}H_2]Cl_2$ and $[(AuOAc)_2(bisNHC^{Bn})]$ (2.1)

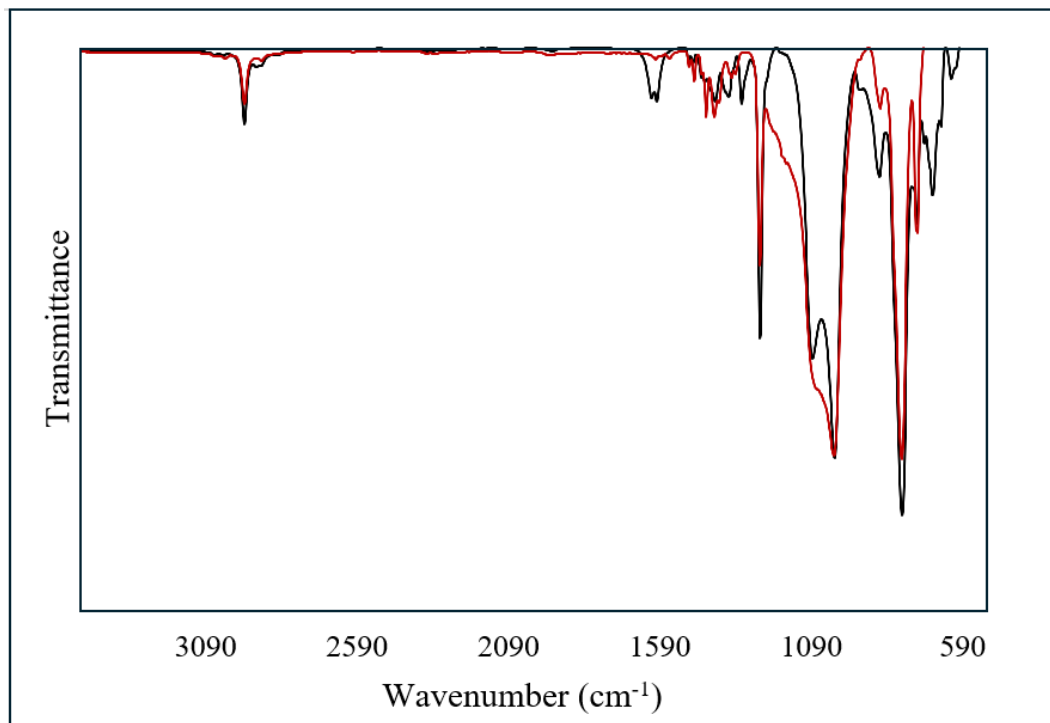


Figure S2.11: FT-IR spectrum of $[(AuOAc)_2(bisNHC^{Bn})]$ (**2.1**) and $[Au_6Se_2(bisNHC^{Bn})_3]^{2+}$ (**2.2**)

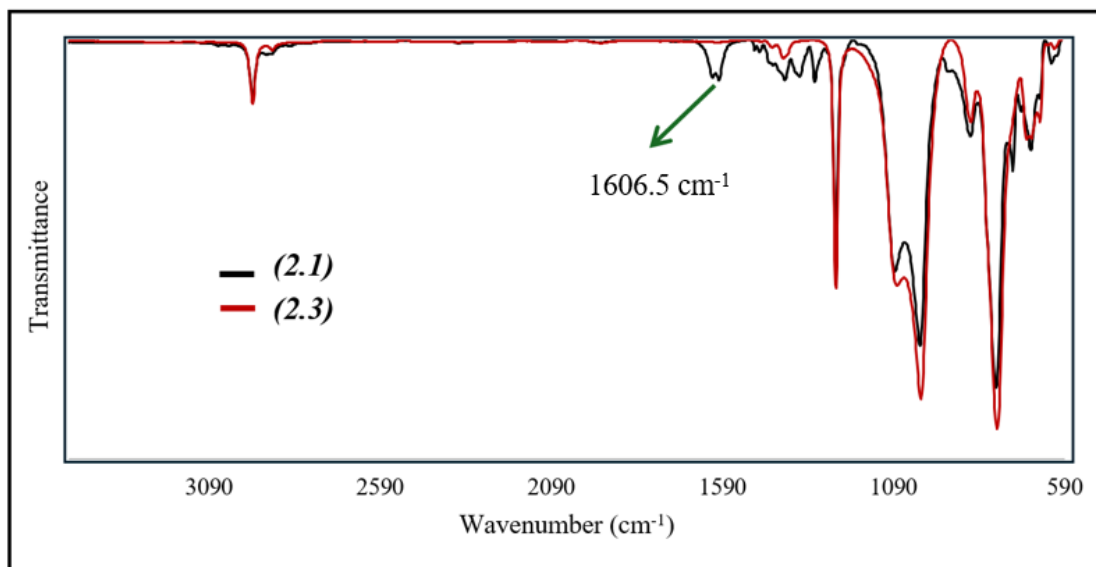


Figure S2.12: FT-IR spectrum of $[(AuOAc)_2(bisNHC^{Bn})]$ (2.1) and $[(AuSePh)_2(bisNHC^{Bn})]$ (2.3)

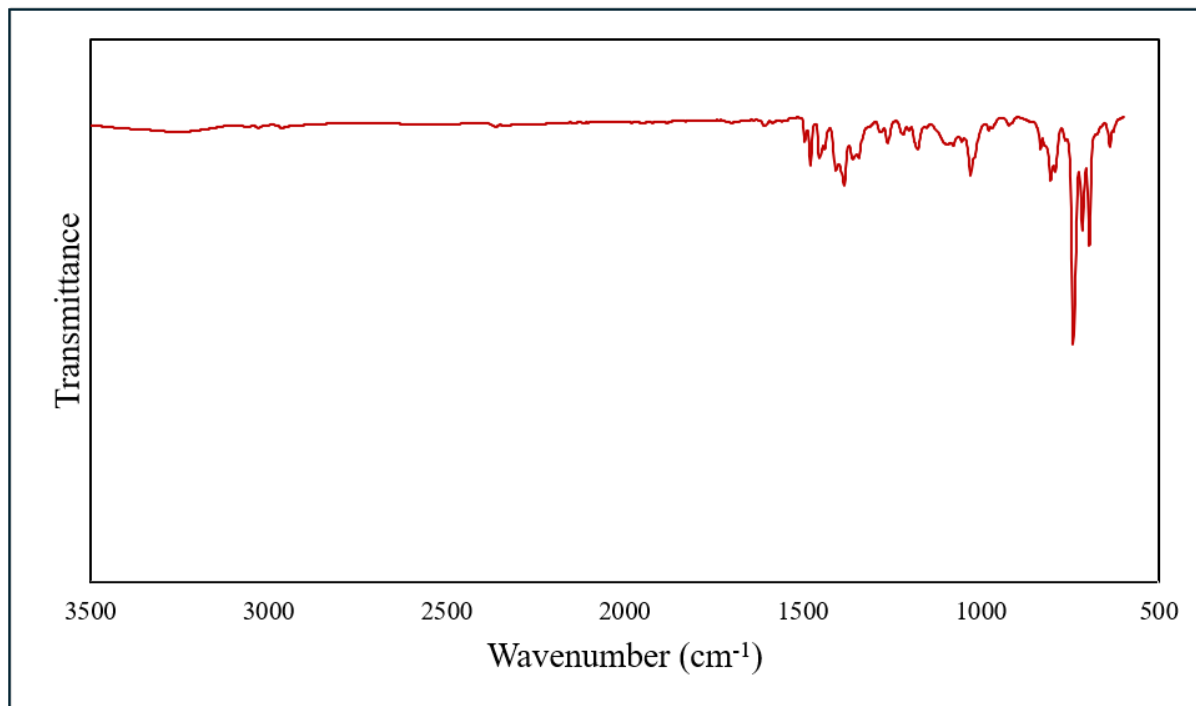


Figure S2.13: FT-IR spectrum of $[(\text{CuCl})_2(\text{bisNHC}^{\text{Bn}})]$ (**2.4**).

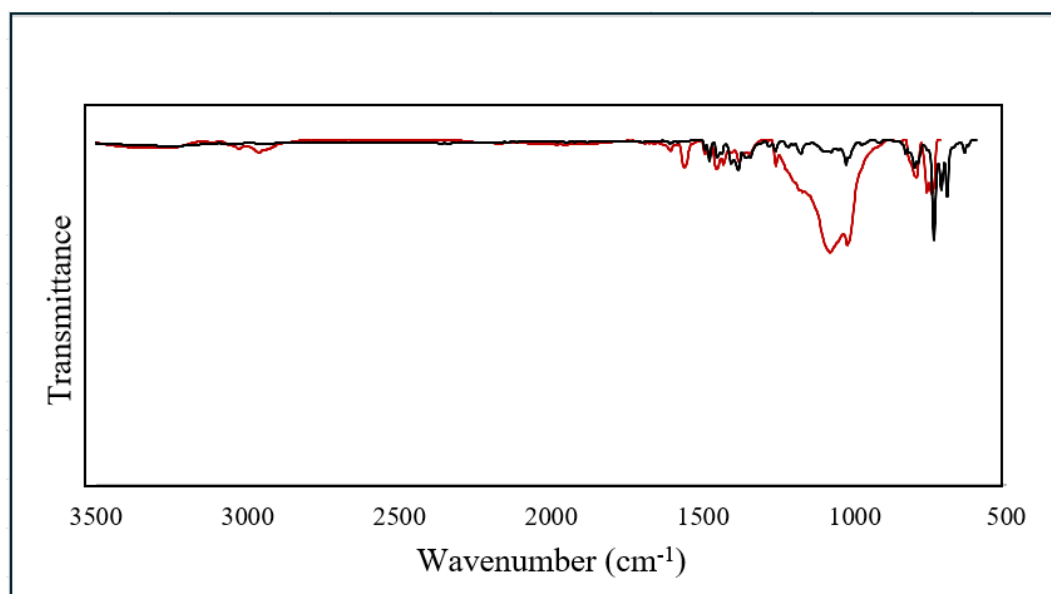


Figure S2.14: FT-IR spectrum of $[(\text{CuCl})_2(\text{bisNHC}^{\text{Bn}})]$ (**2.4**) and copper selenide with $\text{bisNHC}^{\text{Bn}}$ (**2.5**). Black (**2.4**), Red (**2.5**).

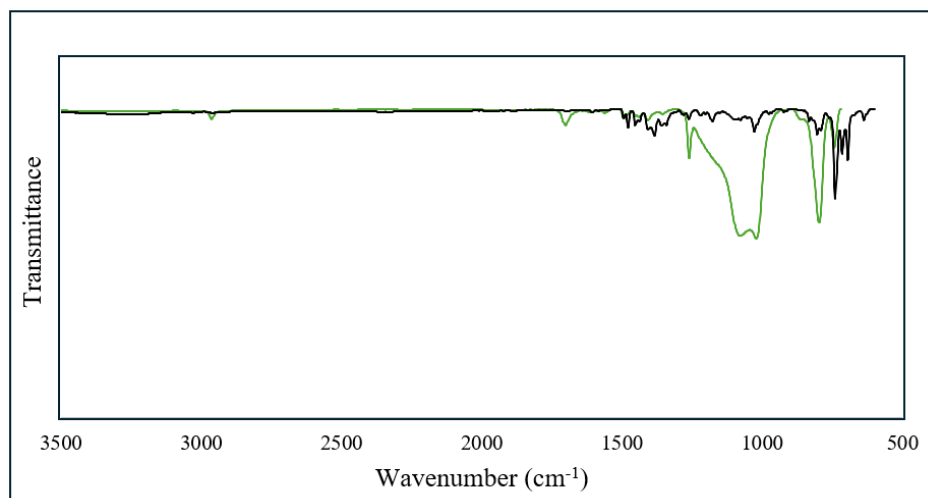


Figure S2.15: FT-IR spectrum of $[(\text{CuCl})_2(\text{bisNHC}^{\text{Bn}})]$ (**2.4**) and copper selenolate with $\text{bisNHC}^{\text{Bn}}$ (**2.6**). Black (**2.4**), Green (**2.6**)

Appendix 1.3: SEM-EDX

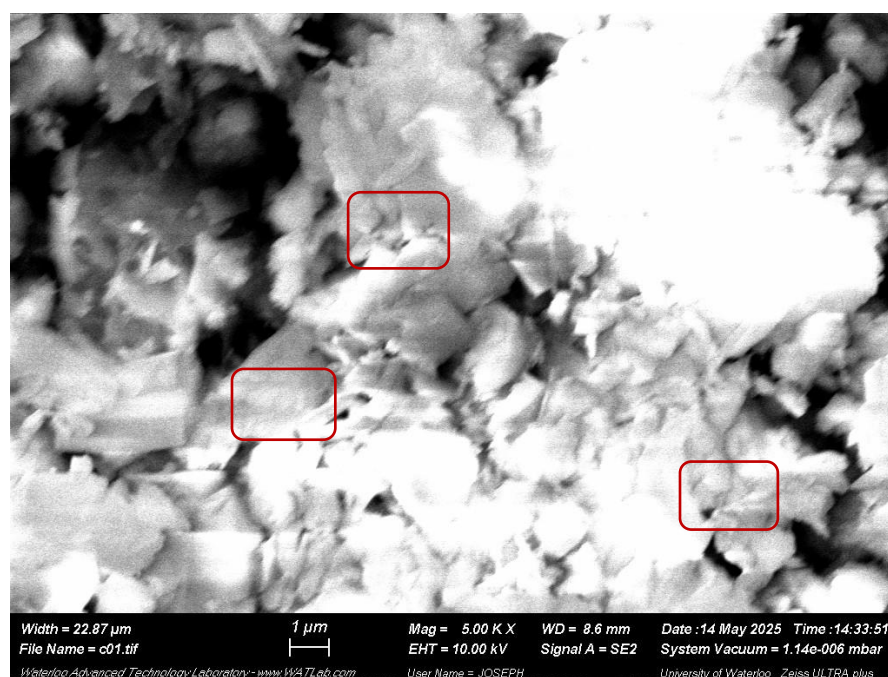
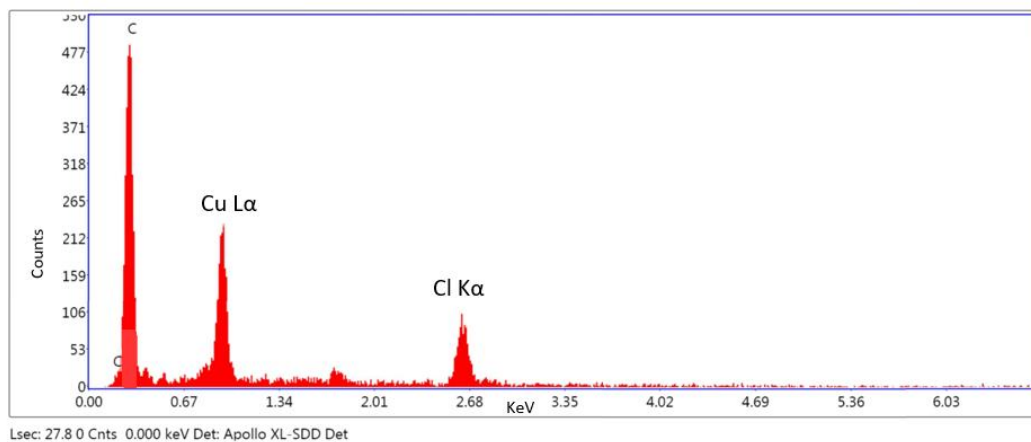


Figure S2.16: Representative EDX spectrum and SEM image of $[(\text{CuCl})_2(\text{bisNHC}^{\text{Bn}})]$ (**2.4**) (three different regions used for the EDX analysis is labelled).

Appendix 1.4: XPS survey

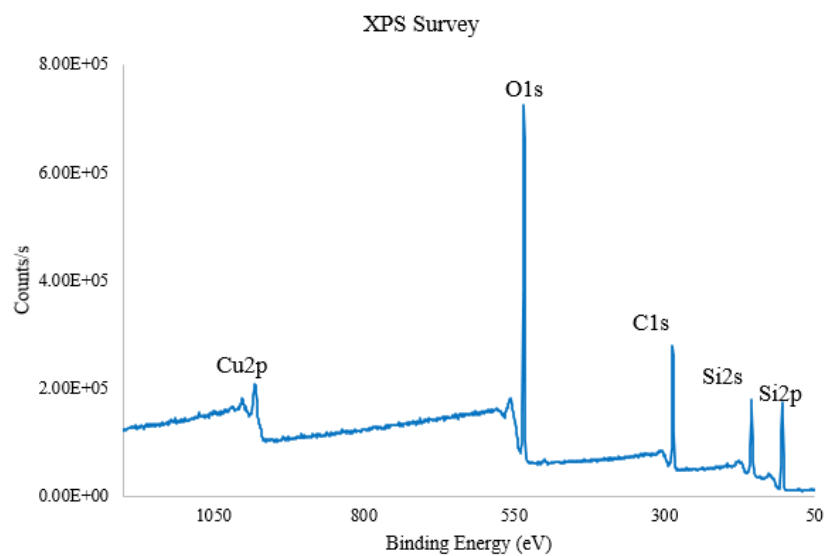


Figure S2.17: XPS survey of copper selenolate with bisNHC^{Bn} (**2.6**).

Appendix 1.5: Mass spectra

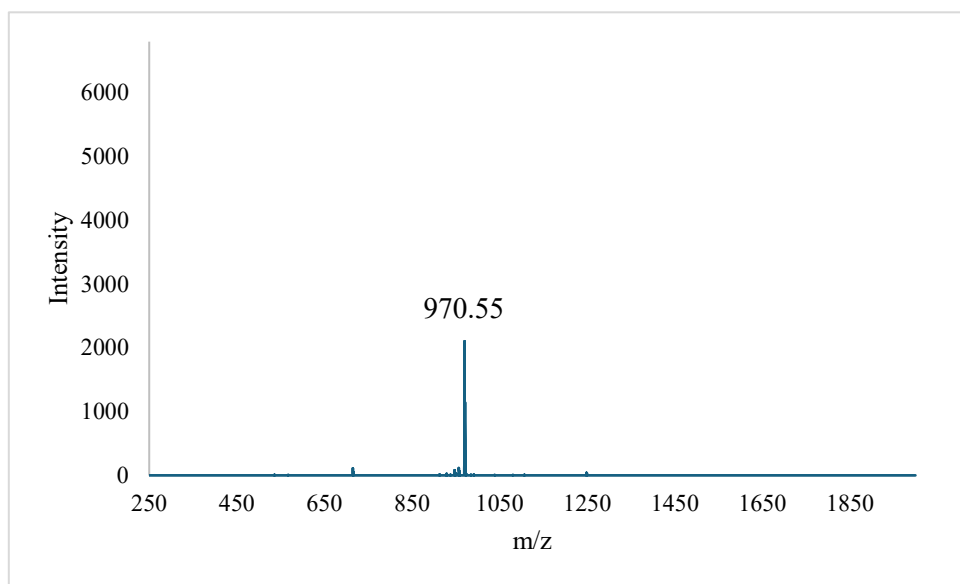


Figure S2.18: Mass spectrum (ESI positive mode) of $[(AuOAc)_2(bisNHC^{Bn})]$ (**2.1**).

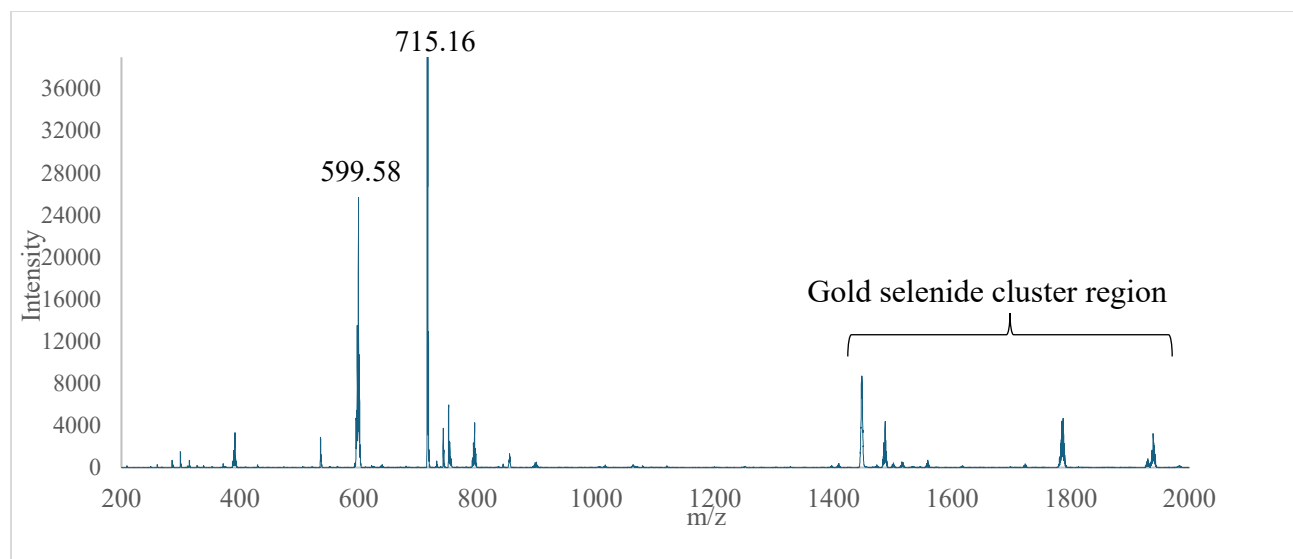


Figure S2.19: Mass spectrum (ESI positive mode) of $[\text{Au}_6\text{Se}_2(\text{bisNHC}^{\text{Bn}})_3]^{2+}$ (**2.2**). (Peak at 599.58 corresponds to $[\text{bisNHC}^{\text{Bn}}\text{-SeH}]^+$ species and the peak at 715.16 is a contaminant possibly from silicon grease).

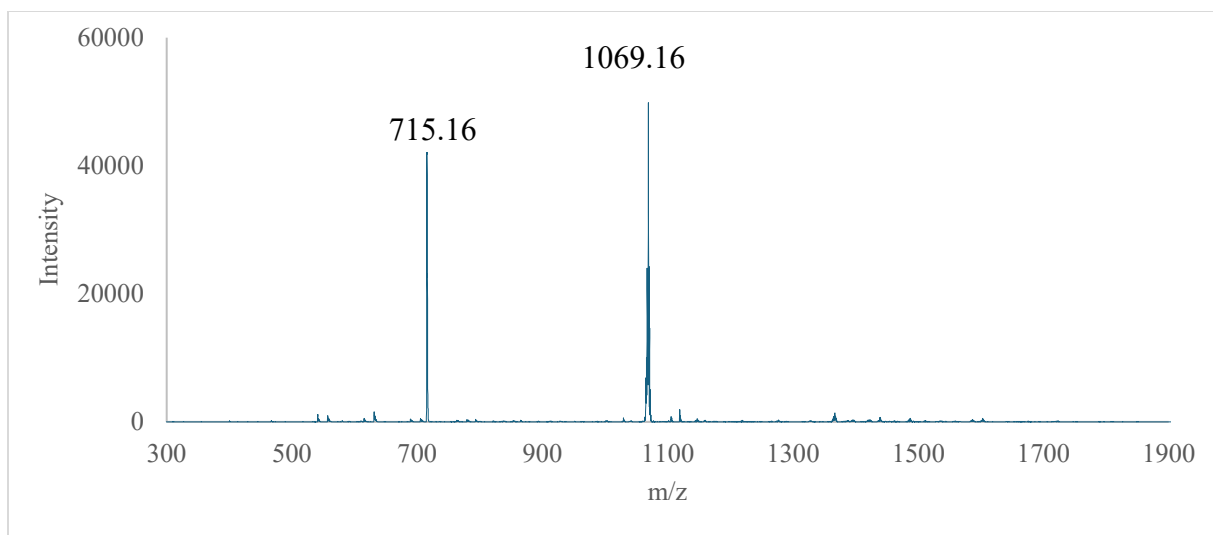


Figure S2.20: Mass spectrum (ESI positive mode) of $[(\text{AuSePh})_2(\text{bisNHC}^{\text{Bn}})]$ (**2.3**). (peak at 715.16 is a contaminant possibly from silicon grease).

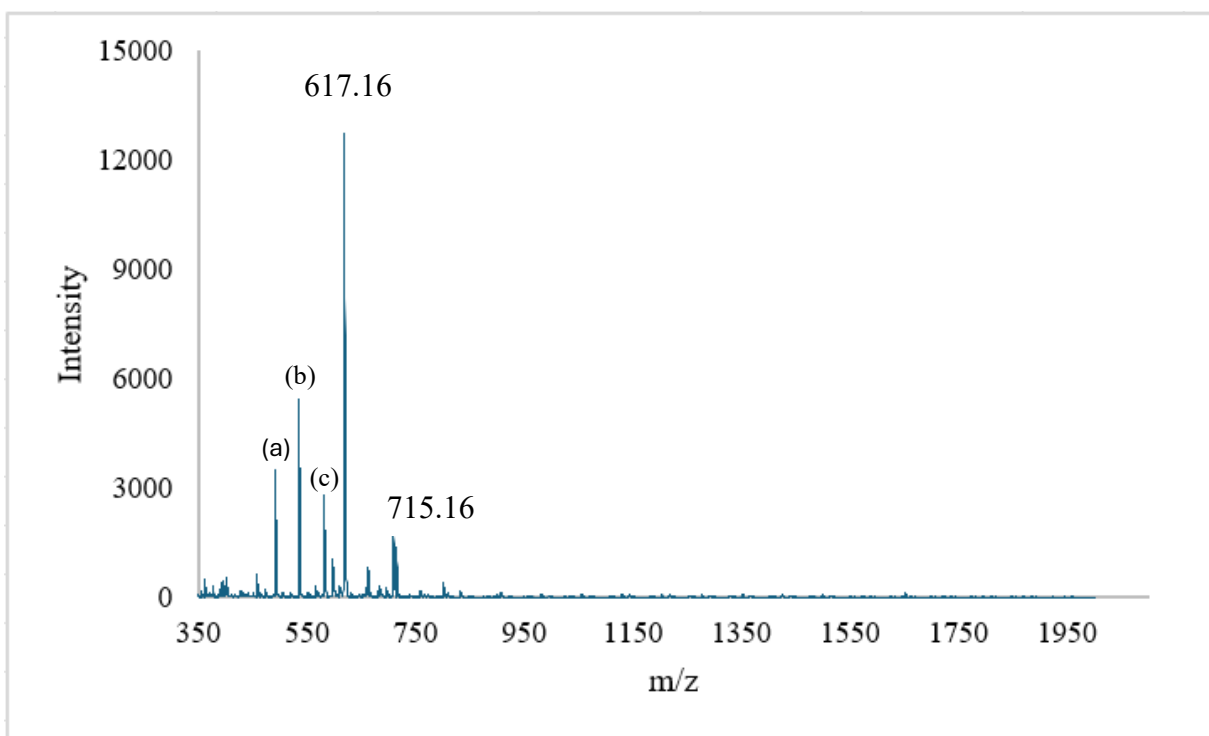


Figure S2.21: Mass spectrum (ESI positive mode) of $[(\text{CuCl})_2(\text{bisNHC}^{\text{Bn}})]$ (**2.4**) obtained from the reaction between $[\text{bisNHC}^{\text{Bn}}\text{H}_2]\text{Cl}_2$ and CuCl (peak at 715.16 is a contaminant possibly from silicon grease).

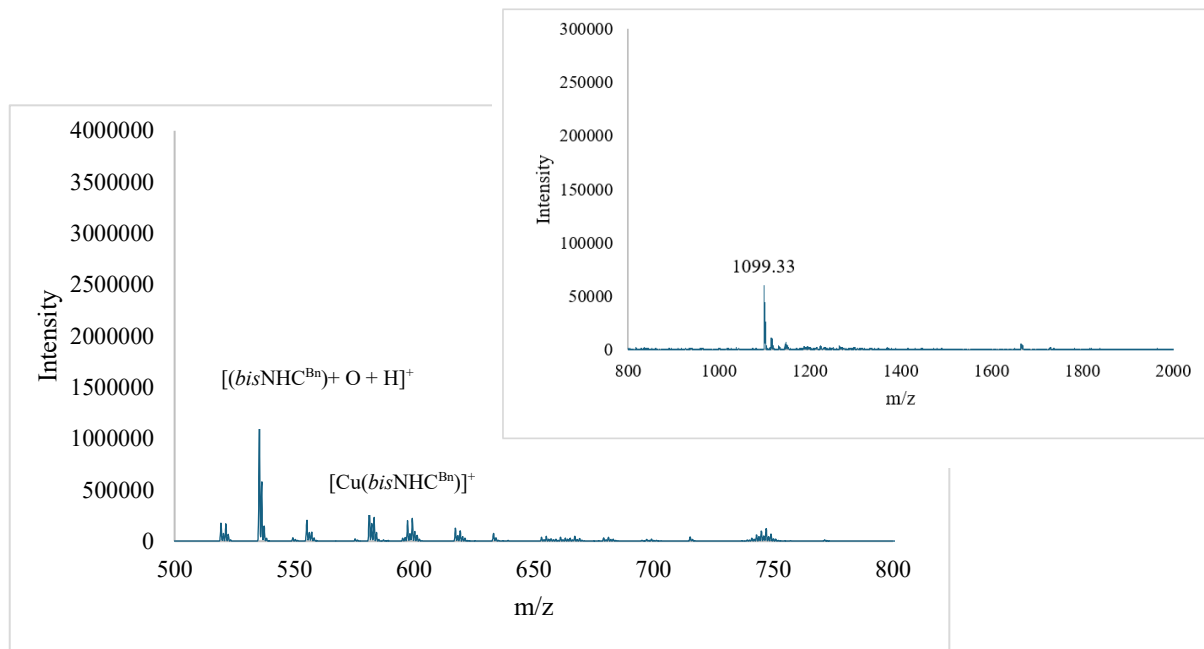


Figure S2.22: Mass spectrum (ESI positive mode) of copper selenide with $bisNHC^{Bn}$ (**2.5**) prepared from the reaction between $[(CuCl)_2(bisNHC^{Bn})]$ (**2.4**) and $Se(SiMe_3)_2$. (High mass region and low mass region is shown separately as the signal of interest (1099.33) is very weak compared to the low mass region signals)