CHEMISTRY OF UNSATURATED ALL THIA AND ALL SELENA DONOR MACROCYCLES: SOME NOTEWORTHY RESULTS

Abstract

Unsaturated thiacrown ethers with *cis*-conformation across the C=C bonds are more conformationally restricted than analogous saturated structures. As a result, they have a high preference for metals when utilised for the formation of metal complexes. In addition, unsaturated selenacrown ethers exhibit a variety of specificity towards metals due to changes in the conformity, diameters, as well as electronegativity. Besides these, role of directional forces are vital in host-guest chemistry. To create three-dimensional architectures containing voids, channels, helices, or networks, such forces are required. Additionally, directional factors are a fundamental prerequisite for the connection involving guests and hosts. Notably crucial ones in pure organic host-guest chemistry are H-bonds and $\pi-\pi$ stacking. A wide range of chalcogen-containing molecules are stacked one on top of the other to form columnar or occasionally tubular stacks. They all have intimate chalcogen-chalcogen solid state interactions in general. In this chapter chemistry of all sulphur/selenium based unsaturated macrocycles have been discussed, mainly their synthesis, metal complex formation and structural details.

Keywords: Selena Donor, Thiacrown.

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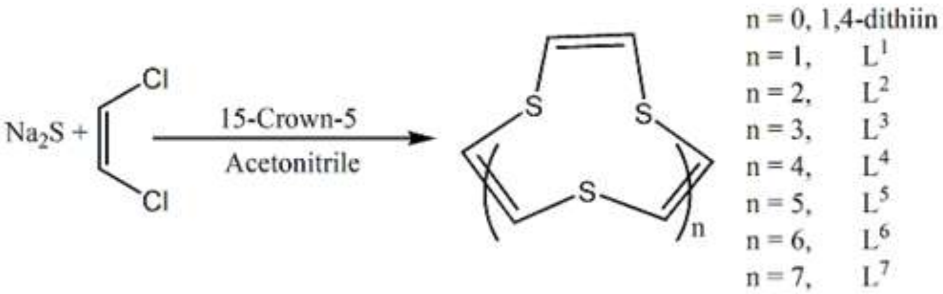
I. INTRODUCTION

The host-guest chemistry of macrocyclic molecules has given rise to the establishment of the field of metal-ion recognition that constitutes one among the many significant coordination chemistry topics to have emerged in the previous several decades. A number of variables, including the size and ionic nature of the metal ion as well as the versatility or cavity dimensions of the macrocycle, have an impact on the chemical nature of metal-ion macrocyclic compounds as well as the shapes these assume in solid form and in a solution. During designing ligands that recognise certain metal ions, each of these aspects are to be put into consideration. Thiacrown ethers, sulfur-substituted crown ethers, experienced major advancements in science throughout the past few decades[1]. Thiacrown ethers are recognised to bind to transition elements, while crown ethers tend to couple towards alkaline as well as alkaline earth metals[2]. This is one of the key distinctions amongst the two types of ethers. On the contrary, compared to equivalent saturated frameworks, unsaturated thiacrown ethers having *cis*- orientation along the carbon-carbon double bonds appear to have been greater conformationally constrained. As a result, it is anticipated that the synthesis of metal compounds using unsaturated thiacrown ethers will exhibit strong selectivity towards metals. Not only thiacrown ether chemistry, scientists have shown immense interest towards selenacrown ethers too. Their chemistry is vastly reported[3]. However, because of variations in the conformity, dimensions, and electronegativity of the chalcogen atoms, unsaturated selenacrown ethers also display varied selectivity against metals. Many instances of pretty mild directional forces governing the architectures of aggregates in solid form may be found in supramolecular chemistry. These forces include, among others, H-bonding as well as $\pi-\pi$ stacking, both of which are being exploited to create channel-like configurations. In the solid state, chalcogen centres in immediate proximity can exert directional forces. Most often close CH······S, C-H·······π–connections, and $\pi-\pi$ stacking occurs hand in hand alongside short SS interconnections. Column-type frameworks are formed by cyclic alkynes, alkenes, as well as alkanes having chalcogen atoms. The intermolecular spacing that separate the chalcogen centres in such columns typically smaller than the total of the van der Waals radii, this is a typical construction motif produced by chalcogen atoms of surrounding stacks. In this chapter, the chemistry of several unsaturated all sulphur and all selenium macrocycles will be discussed in details.

II. UNSATURATED ALL THIA-DONOR MACROCYCLES

Kagimata et. al.[4] reported the synthesis of L^1-L^8 [Scheme 1]. Via the interaction of cis-1,2-dichloroethylene with Na_2S in CH_3CN, unsaturated thiacrown ethers 1,4-dithiin and L^1-L^7 with 6-, 9-, 12-, 15-, 18-, 21-, 24-, and 27- members were produced. All of the sulphur atoms in L^4–L^7 route to the inside of the ring (endodentate), as per the crystalline arrangements of L^3–L^7 [Figure 1]. According to the figures, all the molecules have cavities. The cavities inside L^3-L^7 are, 1.76, 2.34, 3.48, 4.43, and 5.36 Å in size, respectively. The bigger unsaturated thiacrown ethers being oxidised more readily than the smaller systems, as well as unsaturated thiacrown ethers were oxidised more readily than equivalent saturated structures, according to the cyclic voltammograms of L^3-L^7. The colourless complex $[Ag^I(L^3)(CF_3COO)]$ [Figure 1] was produced via the interaction of L^3 with CF_3COOAg in CH_3COCH_3 [Scheme 2]. Three of the five sulphur atoms are shown to be bound to Ag^I in the framework of the crystal.



Scheme 1

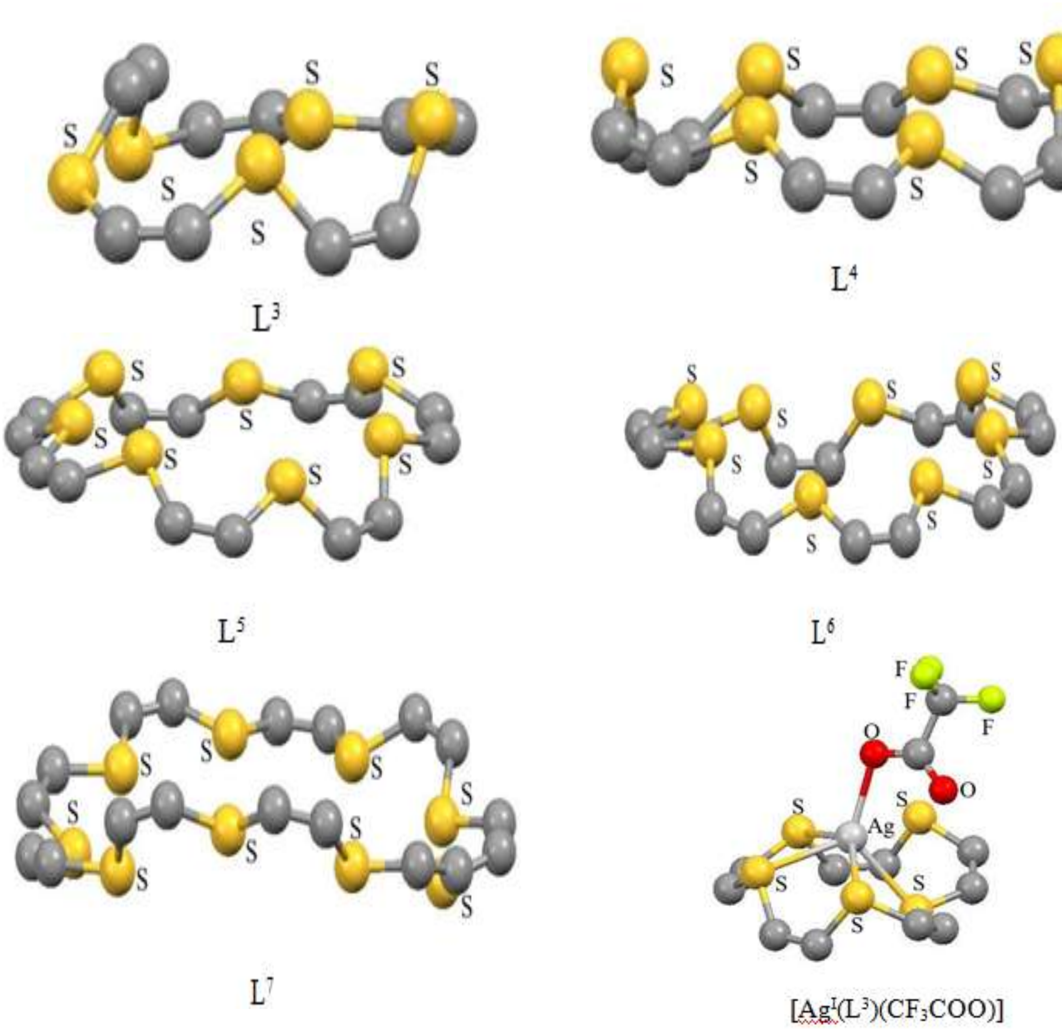
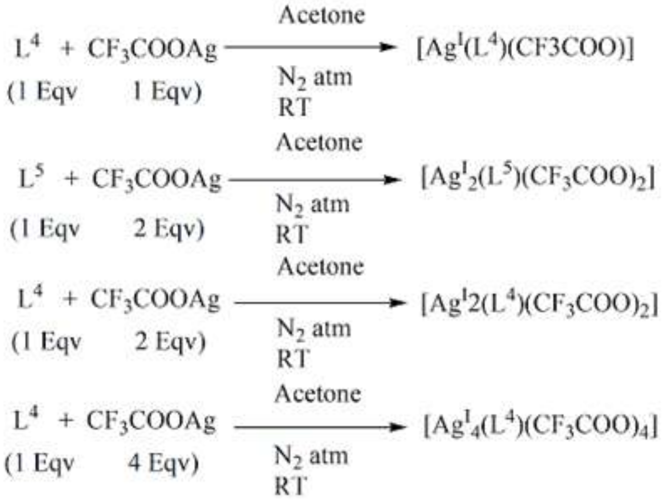


Figure 1

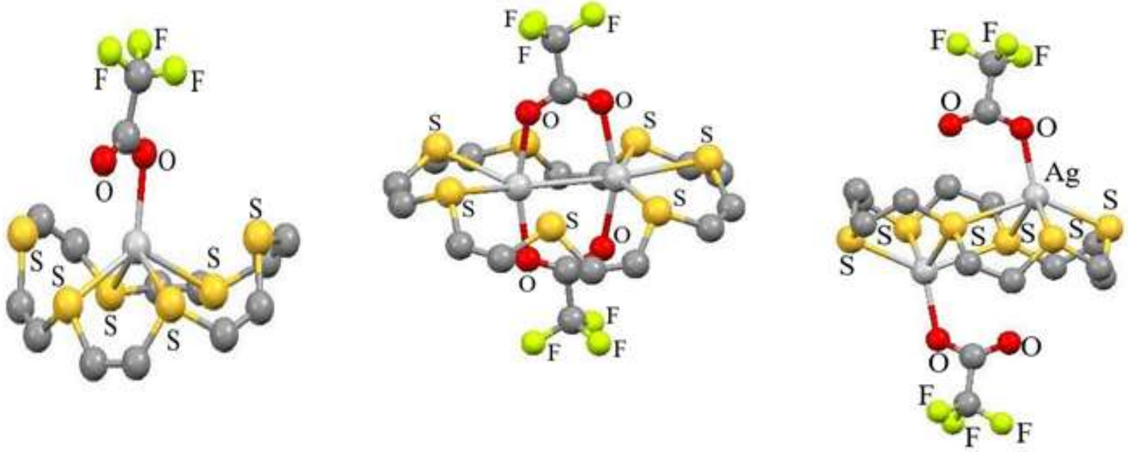
$$L^3 + CF_3COOAg \xrightarrow[N_2\ atm\ RT]{Acetone} [Ag^I(L^3)(CF3COO)]$$

Scheme 2

New Ag^I compounds $[Ag^I(L^4)(CF_3COO)]$ and $[Ag^I_2(L^5)(CF_3COO)_2]$ were produced via the interactions of L^4 and L^5 with silver trifluoroacetate in CH_3COCH_3, respectively[5]. The Ag atom is shown to be located within the cavity of the L^4 and to be surrounded in a distorted square pyramidal configuration in the crystal form of $[Ag^I(L^4)(CF_3COO)]$. The $[Ag^I_2(L^5)(CF_3COO)_2]$ crystal form reveals that all of the sulphur atoms and all of the Ag atoms being roughly coplanar, whereas the two CF_3COO^- units are situated on either side of the plane. By analysing ^1H NMR, the composition of the association of L^3, L^4, and L^5 using CF_3COOAg in solution was investigated. At 1:1 and 2:1 metal to macrocycle proportions, respectively, the titration graphs of L^3 and L^5 exhibit a clear inflection point, while the chart of L^4 progressively varies at a range of 1:1 to 2:1. According to these findings, L^3 and L^5 exhibit inclusion selectivity for the quantity of Ag ions, while L^4 exhibits minimal selectivity for the quantity of metals included. Unsaturated thiacrown ethers turn hard to oxidise by complexing with CF_3COOAg, and CF_3COOAg gets tough to reduce by complexing with unsaturated thiacrown ethers, according to a study comparing the oxidation and reduction potentials for the Ag^I compounds with those of free macrocycles and CF_3COOAg.



Scheme 3



$[Ag^I(L^4)(CF_3COO)]$ $[Ag^I_2(L^5)(CF_3COO)_2]$ $[Ag^I_4(L^4)(CF_3COO)_4]$

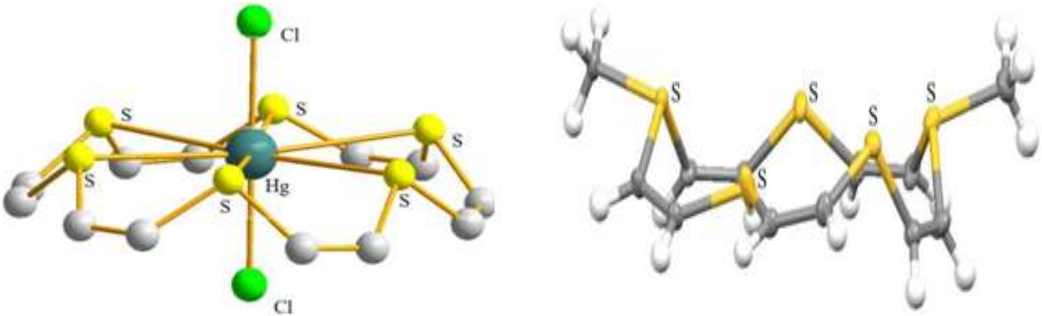
Figure 2

$[Hg^{II}(L^4)Cl_2]$ was produced by complexing L^4 with one equivalent of $HgCl_2$ in CH_3COCH_3. Hg atom was found to be inside the macrocycle's cage and surrounded by an eight-coordinated hexagonal bipyramidal configuration according to the crystal framework of $[Hg^{II}(L^4)Cl_2]$. The results of a ^1H NMR analysis of $[Hg^{II}(L^4)Cl_2]$ in CH_3COCH_3-d_6 showed that the interconversion of unbound L^4 and pure compound occurred more slowly than the time scale of the NMR. According to the ^1H NMR titration study, L^4 demonstrated inclusion selectivity regarding the quantity of Hg atoms[6].

$$L^4 + HgCl_2 \xrightarrow[\text{Nitrogen}\ \text{RT}]{\text{Acetone}} [Hg^{II}(L^4)Cl_2]$$

$$L^5 + HgCl_2 \xrightarrow[\text{Nitrogen}\ \text{RT}]{\text{Acetone}} [Hg^{II}(L^5)Cl_2]$$

Scheme 4

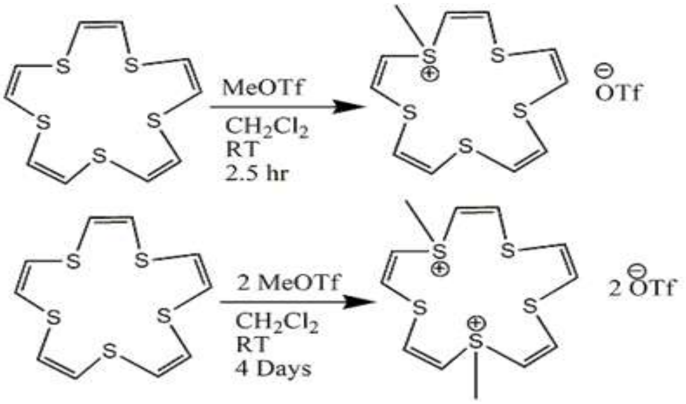


$[Hg^{II}(L^4)Cl_2]$

Dimethylated-L^3

Figure 3

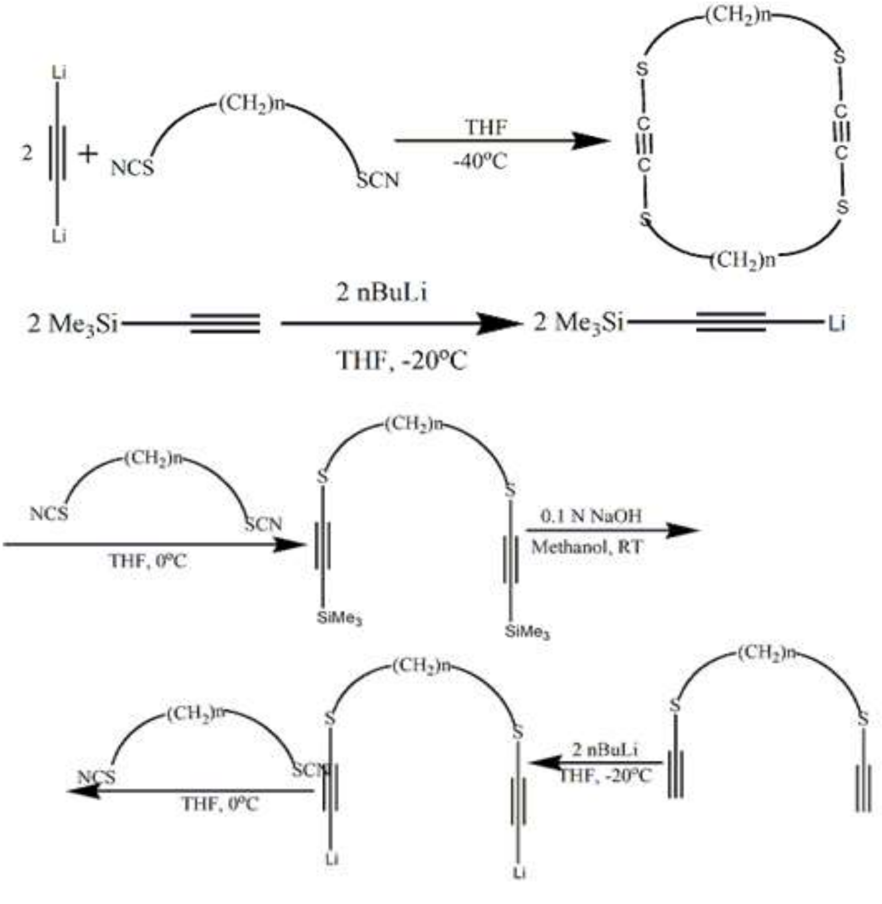
At room temperature, mono- and dimethylated compounds were produced when unsaturated thiacrown ether L^3 and methyl trifluoromethanesulfonate (1 & 2 mmol) in CH_2Cl_2 interacted [Scheme 5]. X-Ray crystallographic study was used to ascertain the dimethylated product's structural architectures[7] [Figure 3].

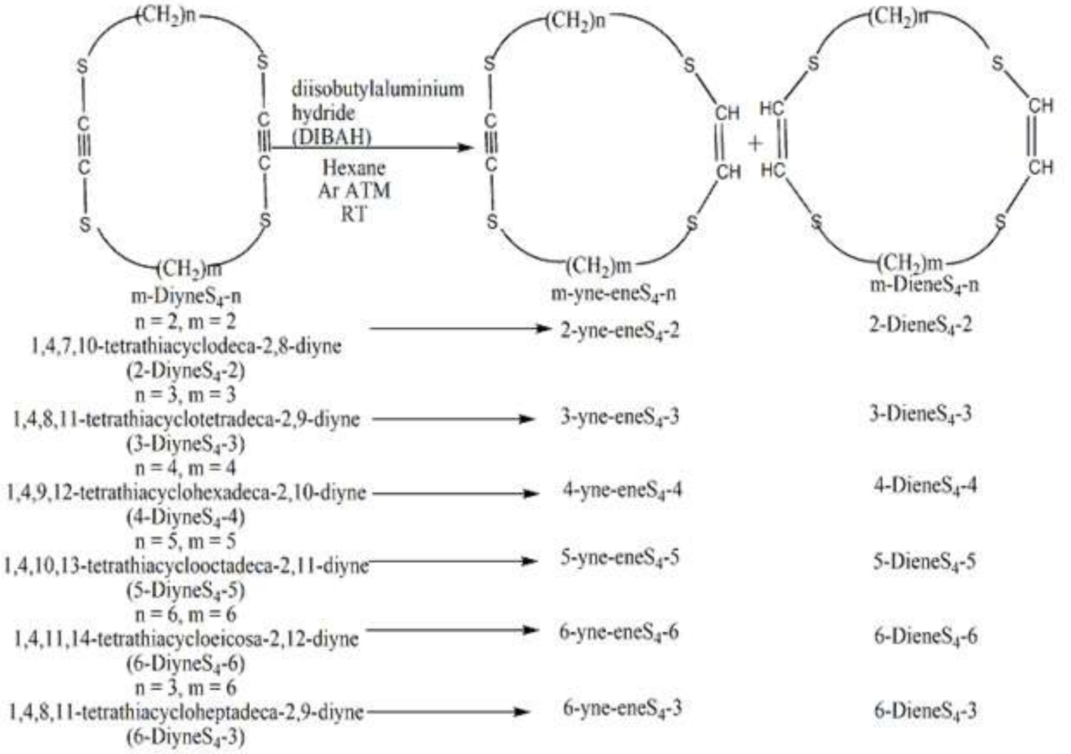


Scheme 5

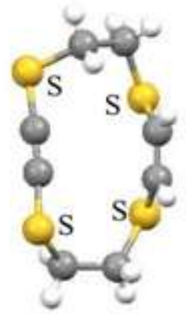
Electron transfer mechanism causes the 15-, 18-, 21-, and 24-membered unsaturated thiacrown ethers (L3-L6) to create 1:1 combinations in solution containing the lanthanum metallofullerene La@C82. L5 possesses the most favourable ring diameter in terms of association with La@C82 among the aforementioned unsaturated thiacrown ethers. It is shown that the association efficiency towards La@C82 varies with the dimension of the thiacrown ethers as the host molecules, indicating the generation of inclusion compounds[8].

Diisobutylaluminium Hydride (DIBAH) was used by researchers to precisely reduce the triple bonds of a number of cyclic diynes: 1,4,7,10-tetrathiacyclodeca-2,8-diyne (2-DiyneS_4-2), 1,4,8,11-tetrathiacyclotetradeca-2,9-diyne (3-DiyneS_4-3), 1,4,9,12-tetrathiacyclohexadeca-2,10-diyne (4-DiyneS_4-4), 1,4,10,13-tetrathiacyclooctadeca-2,11-diyne (5-DiyneS_4-5), 1,4,11,14-tetrathiacycloeicosa-2,12-diyne (6-DiyneS_4-6) and 1,4,8,11-tetrathiacycloheptadeca-2,9-diyne (6-DiyneS_4-3). It was possible to separate and characterise the consequent cyclic enynes as well as cyclic dienes. Most of them were characterized by X-Ray crystallography also [2-yne-eneS_4-2, 4-yne-eneS_4-4, 5-yne-eneS_4-5, 2-DieneS_4-2 to 6-DieneS_4-3]. Stair-like configurations were discovered for all molecular arrangements. The stiff structure units (S-CH=CH-S and/or (S-C≡C-S) and the zigzag orientations of the chains of hydrocarbons were the source of these molecular structures. Column-like features in the solid-state versions of 5-yne-eneS_4-5, 3-DieneS_4-3, 4-DieneS_4-4, and 5-DieneS_4-5 that were imposed on by close interactions between the sulphur centres of nearby rings were seen[9].

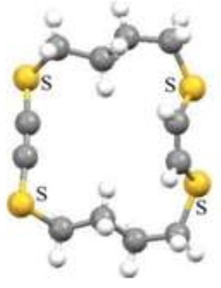




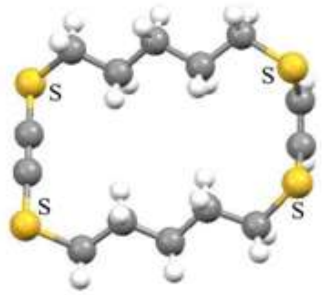
Scheme 6



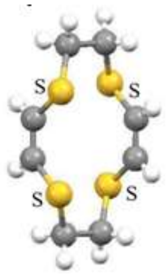
2-yne-eneS_4-2



4-yne-eneS_4-4



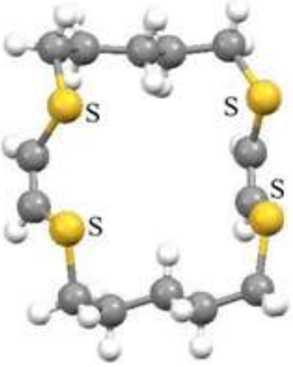
5-yne-eneS_4-5



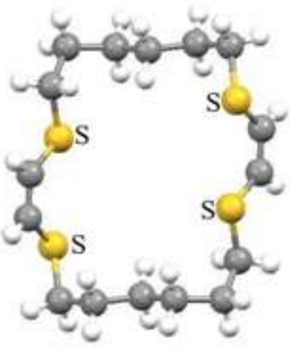
2-DieneS_4-2

3-DieneS_4-3

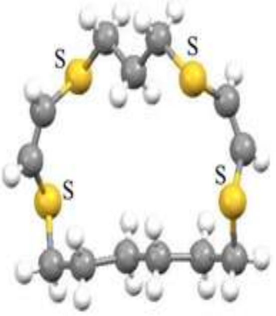
4-DieneS_4-4



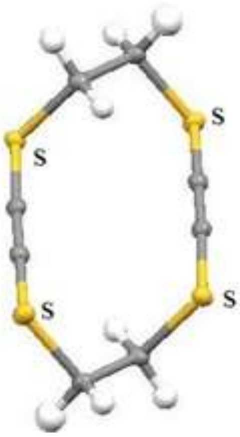
5-DieneS$_4$-5



6-DieneS$_4$-6

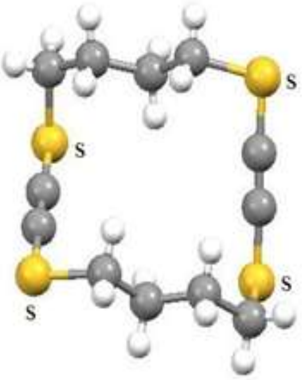


6-DieneS$_4$-3

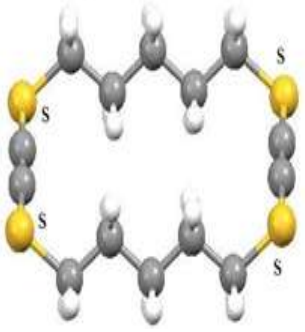


2-DiyneS$_4$-2

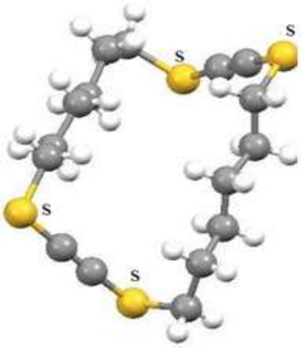
DiyneS$_4$-3



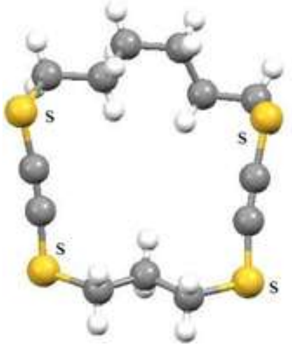
4-DiyneS$_4$-4



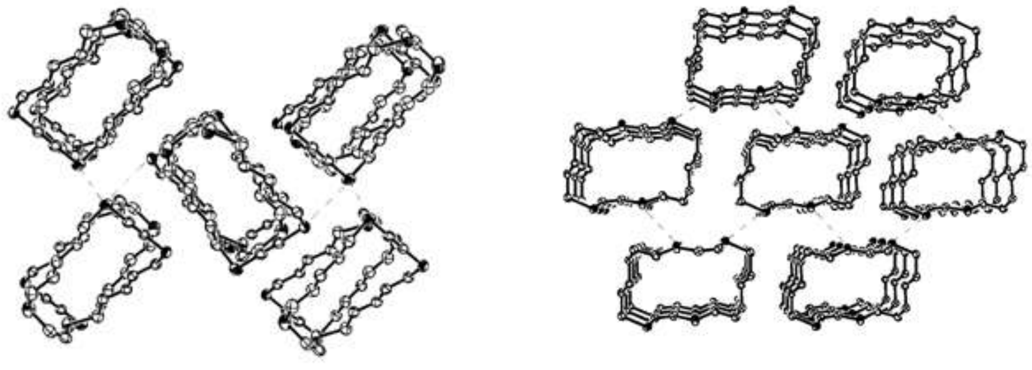
5-DiyneS$_4$-5



6-DiyneS$_4$-6



6-DiyneS$_4$-3



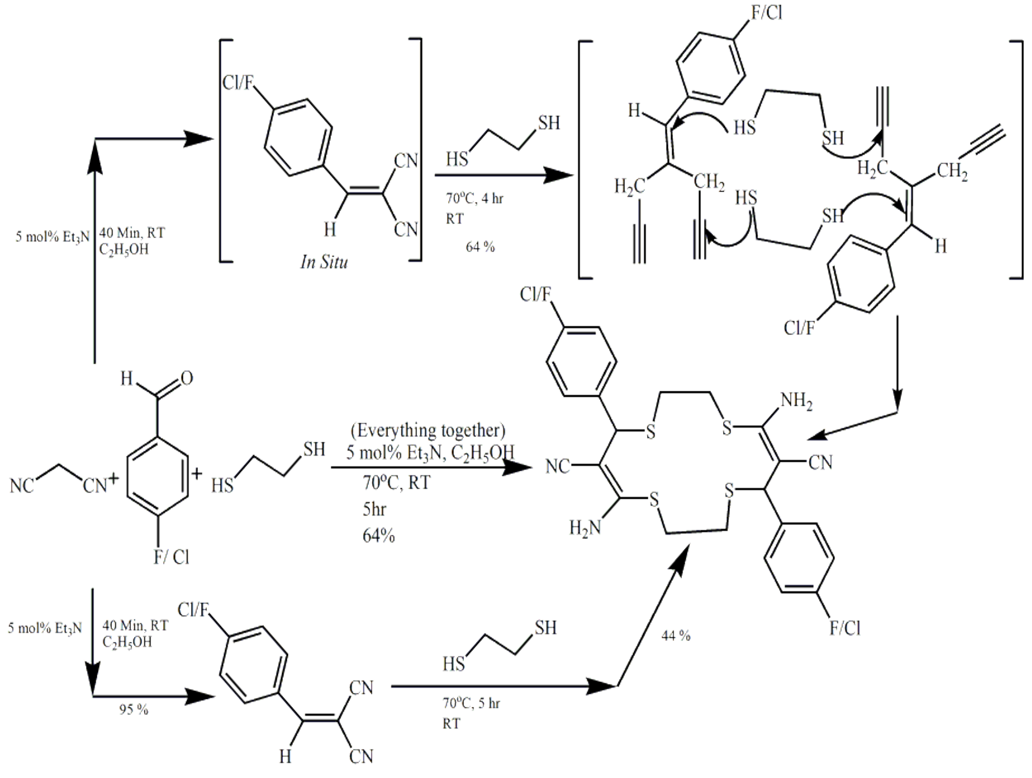
Columnar structure of 5-DieneS_4-5

Columnar structure of 6-DieneS_4-6

Figure 4

Several similar types of Diyne-, tetrayne- and hexayne- systems will be discussed in details inside related sections for selenium later in this chapter.

Malononitrile, aryl aldehydes, and 1,2-ethanedithiol were all used in the multicomponent macroheterocyclization to generate 5,12-diamino-7,14-bis(aryl)-1,4,8,11-tetrathiacyclotetradeca-5,12-diene-6,13- dicarbonitriles in presence of catalytic quantity of Et_3N in EtOH [Scheme 7]. By using spectroscopic techniques, the geometry of the generated macroheterocycles was verified[10].



Scheme 7

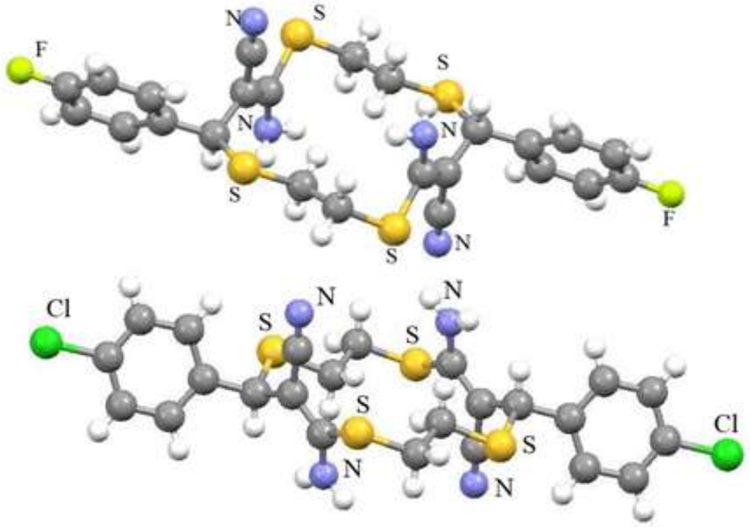
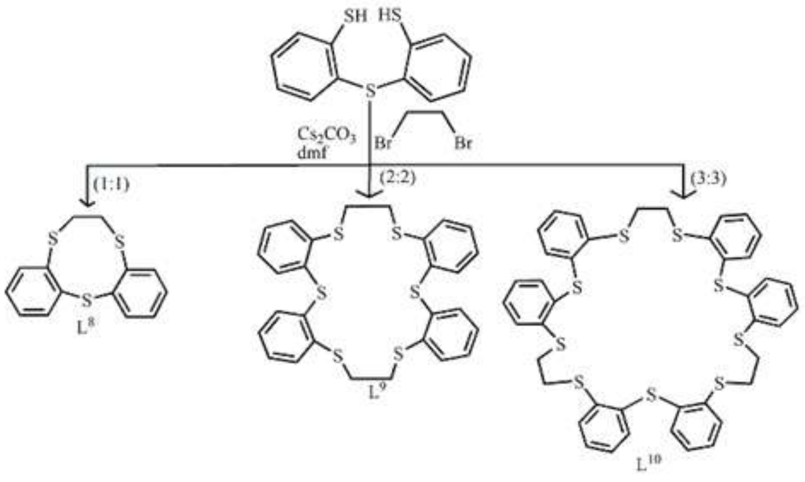
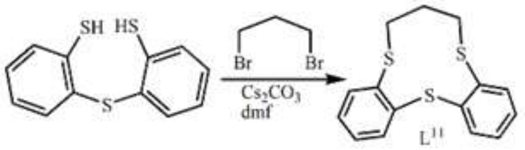
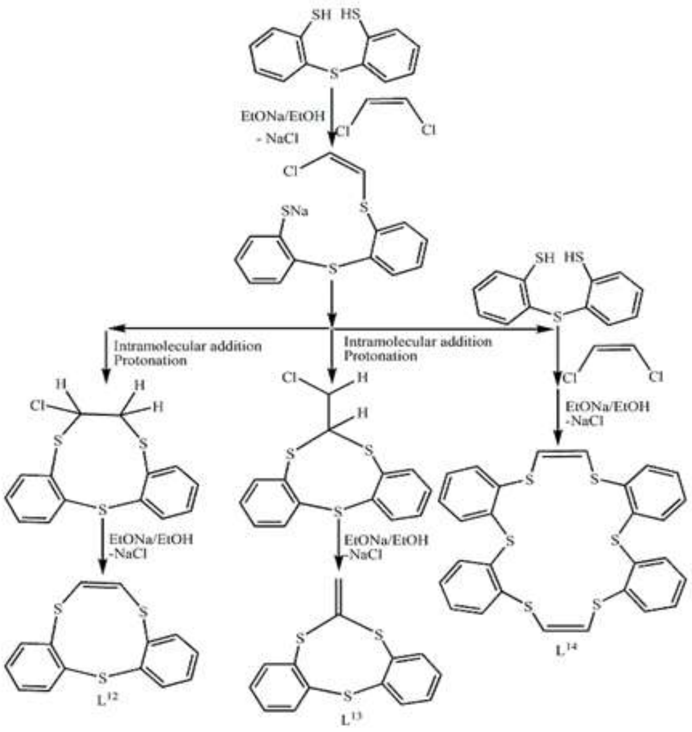


Figure 5

In the presence of Caesium Carbonate in N, N-dimethyl formamide, bis(o-mercaptophenyl) sulphide combined with 1,2-dibromoethane to produce the 9-membered-ring 1:1-condensed resultant compound (L^{8}), the 18-membered ring 2:2 condensed item (L^{9}), as well as the 27-membered ring 3:3 condensed final compound (L^{10}), having yields of 42, 19, and 5%, respectively. The 10-membered ring 1:1 condense result (L^{11}) was the only discernible product in a 42% yield following the condensation of Bis(o-mercaptophenyl) sulphide with 1,3-dibromopropane. Two isomeric 1:1-condensation compounds with yields of 25% (L^{12}) and 5% (L^{13}), respectively, were produced by the reaction of Bis(o-mercaptophenyl) sulphide with cis-1,2-dichlorocthylene in refluxing Ethanol in the presence of EtONa, as well as the 2:2 condense compound (20%) (L^{14})[11].







Scheme 8

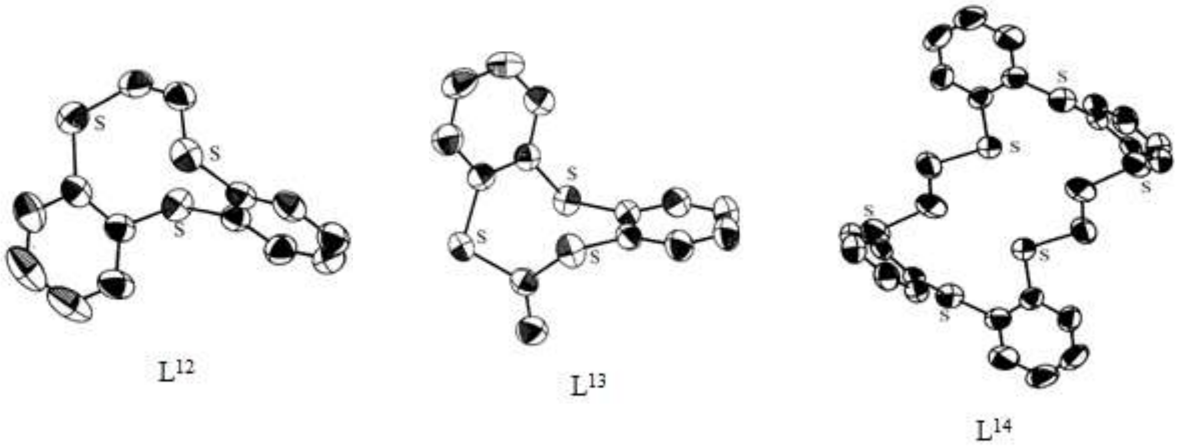
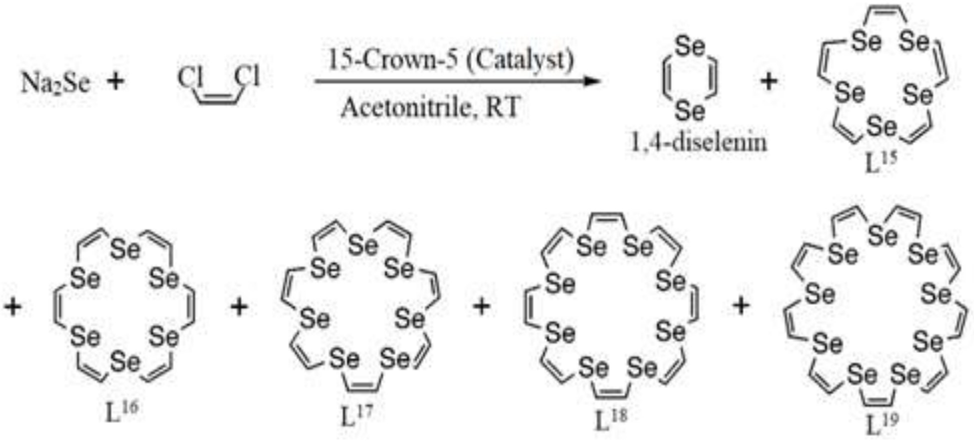


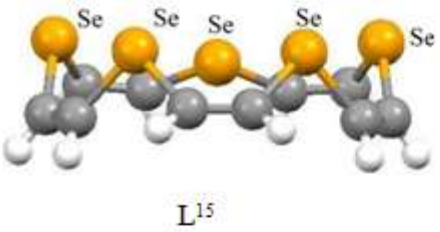
Figure 6

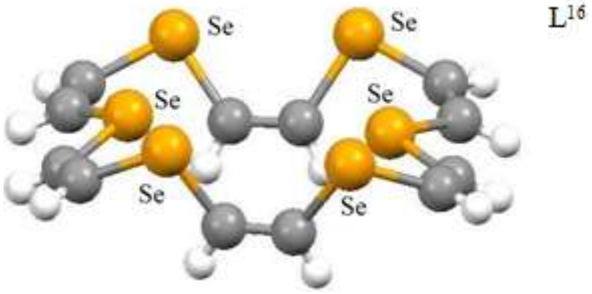
III. UNSATURATED ALL SELENA-DONOR MACROCYCLES

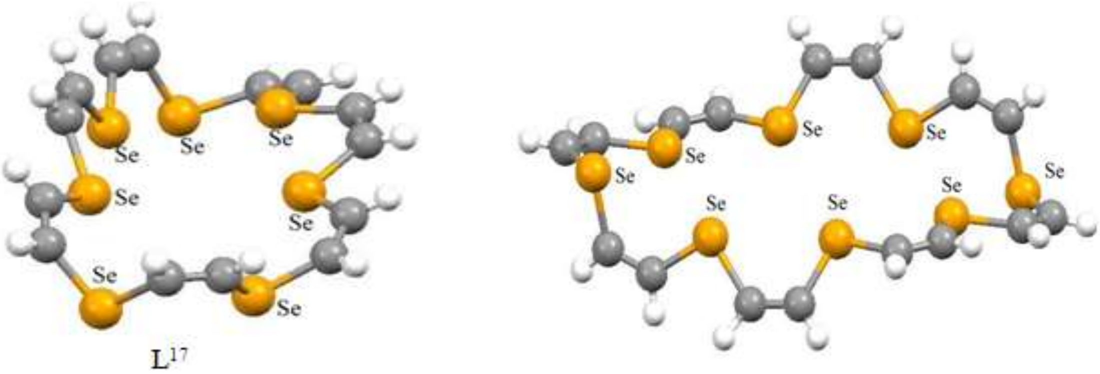
In the beginning Kamigata et al.[12,13] produced 1,4-diselenin and unsaturated selenacrown ethers L^{15}–L^{19} [Scheme 9]. Because of the unfavourable conformation in the ring closing reaction, the 9- and 12-member unsaturated selelacrown ethers cannot be generated by the aforementioned procedure. The respective energy of the 9- and 12-member molecules are greater compared to that of the remaining selenacrown ethers, according to calculations of molecular orbitals[13]. The C=C bonds across each of the L^{15}–L^{18} crystal frameworks have *cis-* conformations, and all of the Se atoms are pointed in the direction of the cavities. While the frameworks of the related unsaturated thiacrown ethers get rounder as the dimension increases[4], the molecular frameworks of the rings get more elliptically narrow here. The larger unsaturated selenacrown ethers being more readily oxidised than the smnaller ones, according to the cyclic voltammograms. Because the C-Se bonds are weaker than those of the C-S bonds, unsaturated selenacrown ethers being thermally more unstable than their equivalent sulphur counterparts[13]. The following compounds were synthesized: $[Ag(1,4\text{-diselenin})(CF_3COO)]$, $[Ag(1,4\text{-diselenin})_2(CF_3COO)]$, $[Ag(L^{15})(CF_3COO)]$, $[Ag_5(L^{16})3(CF_3COO)_5]$, $[Ag_7(L^{17})(CF_3COO)_5]$, $[Ag(L^{18})(CF_3COO)]$, $[Ag_2(L^{18})(CF_3COO)_2]$, $[Ag_3(L^{18})_2(CF_3COO)_3]$, $[Ag(L^{15})(NO_3)]$ and $[Ag(L^{17})(BF_4)]$ [Scheme 10]. Crystal structure of $[Ag(1,4\text{-diselenin})_2(CF_3COO)]$, $[Ag(L^{15})(CF_3COO)]$, $[Ag(L^{15})NO_3]$, $[Ag_2(L^{18})(CF_3COO)_2]$ and $[Ag_5(L^{16})_3(CF_3COO)_5]$ are shown in Figure 8. One Ag atom exists within the macrocycle cavity of $[Ag(L^{15})(CF_3COO)]$. This results in a deformed 5-coordinated square pyramidal configuration surrounding the Ag atom, linked by three Se atoms, one O atom that comes from the CF_3COO^- group, and another loosely bound Se atom. $[Ag(L^{15})(NO_3)]$ shares structural similarities with $[Ag(L^{15})(CF_3COO)]$. Out of the three crown components in $[Ag_5(L^{16})_3(CF_3COO)_5]$, one L^{16} has one Ag atom while the remaining two macrocycles contain two Ag atoms, respectively. In accordance with the arrangement of $[Ag_2(L^{18})(CF_3COO)_2]$, one L^{18} unit's cavity contains two Ag atoms. Two of each CF_3COO^- group's O atoms coordinate with different Ag atoms. The two CF_3COO^- units are situated on different sides of the ring plane. Unsaturated selenacrown ether's in-solution Ag ion inclusion behaviour was studied. At low concentrations in solution, the unsaturated Se-ether predominantly produces 1:1 compounds.



Scheme 9







L^{17} L^{18}

Figure 7

$$\text{1,4-diselenin} + CF_3COOAg \xrightarrow[\substack{N_2\ \text{ATM}\\ \text{RT}}]{\text{Acetone}} [Ag(\text{1,4-diselenin})(CF_3COO)]$$

$$\underset{(2\ \text{eqv.})}{\text{1,4-diselenin}} + CF_3COOAg \xrightarrow[\substack{N_2\ \text{ATM}\\ \text{RT}}]{\text{Acetone}} [Ag(\text{1,4-diselenin})_2(CF_3COO)]$$

$$L^{15} + CF_3COOAg \xrightarrow[\substack{N_2\ \text{ATM}\\ \text{RT}}]{\text{Acetone}} [Ag(L^{15})(CF_3COO)]$$

$$L^{16} + \underset{(2\ \text{eqv.})}{CF_3COOAg} \xrightarrow[\substack{N_2\ \text{ATM}\\ \text{RT}}]{\text{Acetone}} [Ag_5(L^{16})_3(CF_3COO)_5]$$

$$L^{17} + \underset{(4\ \text{eqv.})}{CF_3COOAg} \xrightarrow[\substack{N_2\ \text{ATM}\\ \text{RT}}]{\text{Acetone}} [Ag_7(L^{17})(CF_3COO)_5]$$

$$L^{18} + CF_3COOAg \xrightarrow[\substack{N_2\ \text{ATM}\\ \text{RT}}]{\text{Acetone}} [Ag(L^{18})(CF_3COO)]$$

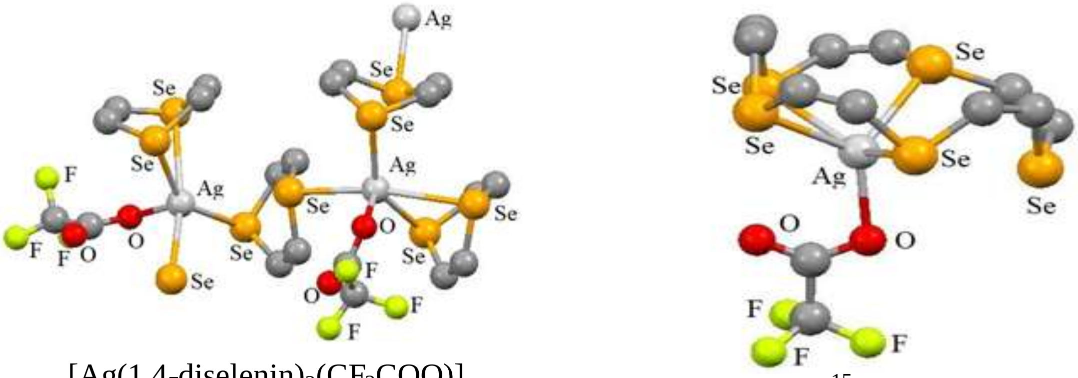
$$L^{18} + \underset{(2\ \text{eqv})}{CF_3COOAg} \xrightarrow[\substack{N_2\ \text{ATM}\\ \text{RT}}]{\text{Acetone}} [Ag_2(L^{18})(CF_3COO)_2]$$

$$L^{18} + \underset{(3\ \text{eqv})}{CF_3COOAg} \xrightarrow[\substack{N_2\ \text{ATM}\\ \text{RT}}]{\text{Acetone}} [Ag_3(L^{18})_2(CF_3COO)_3]$$

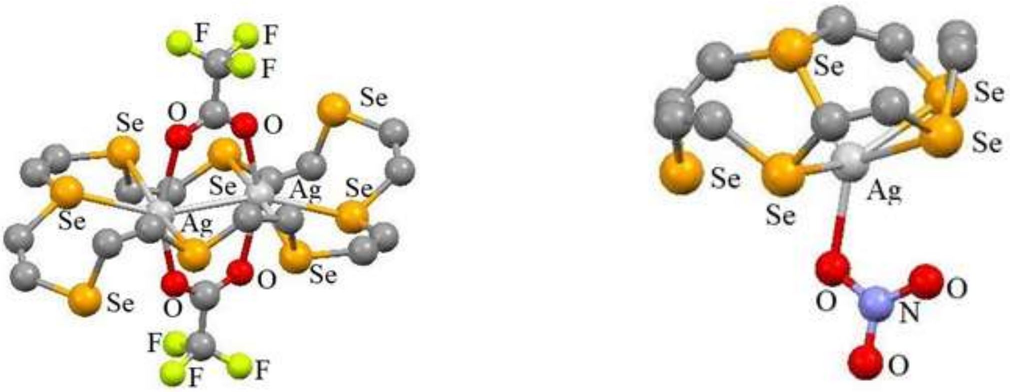
$$L^{15} + AgNO_3 \xrightarrow[\substack{N_2\ \text{ATM}\\ \text{RT}}]{\text{Acetone}} [Ag(L^{15})(NO_3)]$$

$$L^{17} + \underset{(2\ \text{eqv.})}{AgBF_4} \xrightarrow[\substack{N_2\ \text{ATM}\\ \text{RT}}]{\text{Acetone}} [Ag(L^{17})(BF_4)]$$

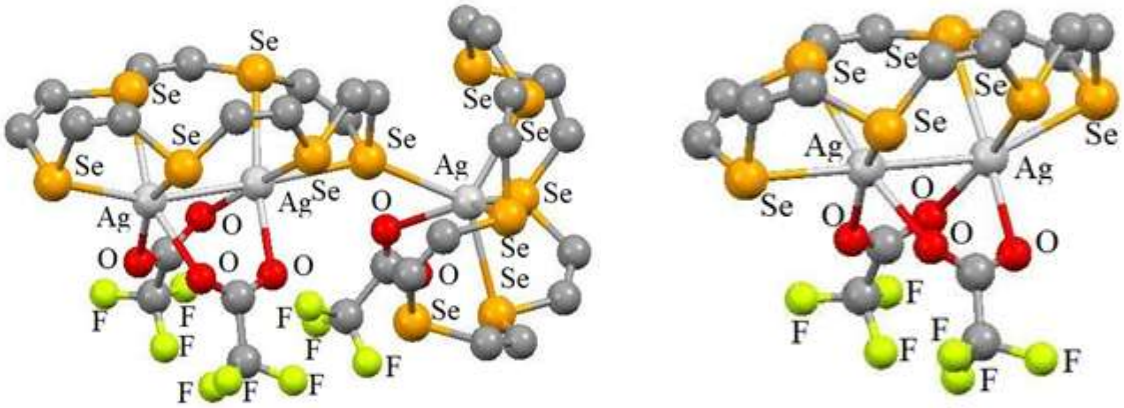
Scheme 10



$[Ag(1,4\text{-diselenin})_2(CF_3COO)]$ $[Ag(L^{15})(CF_3COO)]$



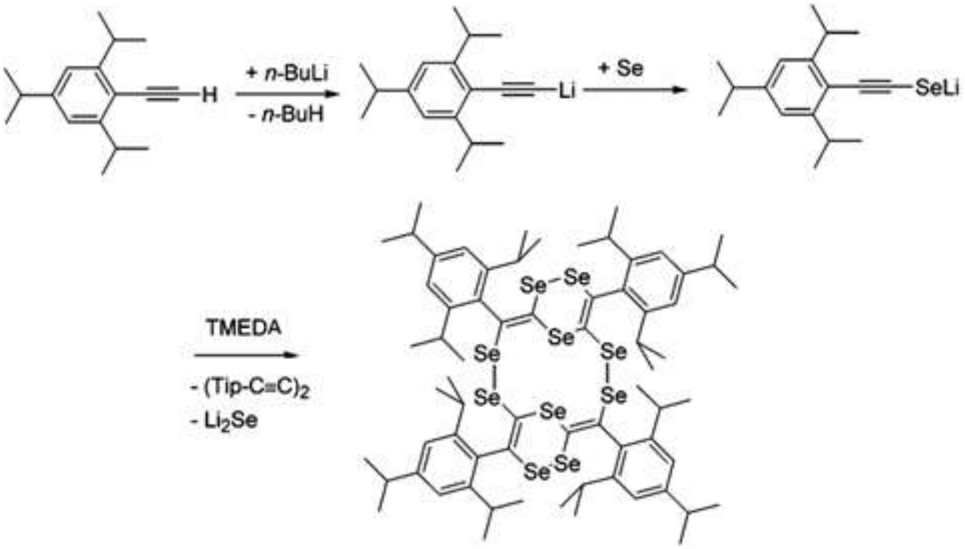
$[Ag_2(L^{18})(CF_3COO)_2]$ $[Ag(L^{15})NO_3]$



$[Ag_5(L^{16})_3(CF_3COO)_5]$

Figure 8

Sterically crowded compound Lithium 2,4,6- triisopropylphenylalkynylselenolate is produced when 2,4,6-triisopropylphenylethynyllithium reacts with grey selenium (Scheme 11). This compound is reactive in solution and proceeds self-addition to produce an unusually Se-rich macrocycle. Tetramethylethylenediamine and other coordinating chemicals appeared to significantly speed up the process. The macroheterocycle's architecture (Figure 9) revealed two outside six-membered rings connected to a centre 12-member ring. The only components of the rings' robust tricyclic backbone are quaternary alkenylidene and Se. This Se-enriched macrocycle has very little flexibility due to the positioning of the alkenylidene groups[14].



Scheme 11

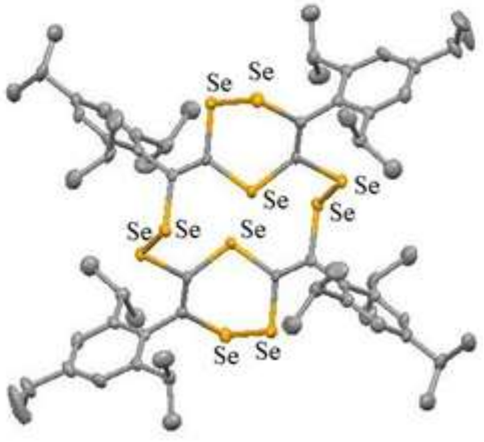
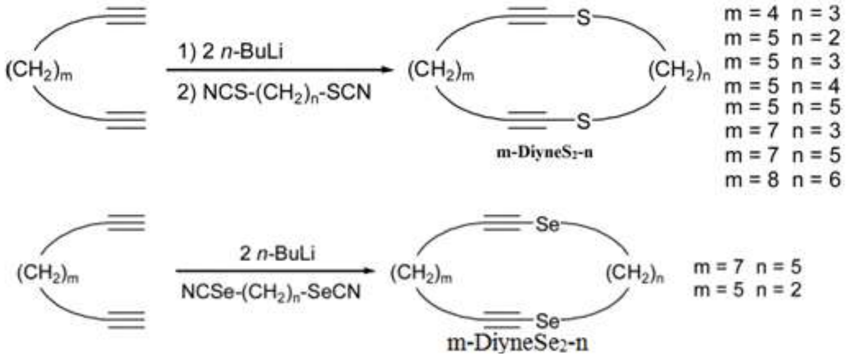


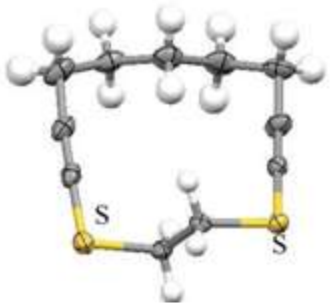
Figure 9

The generation of cyclic diynes with the general composition m-DiyneX_2-n [X = S. Se] was described by Gleiteret al.[15] The chains that separate two C≡C-Se units are denoted by the letters m and n. The bridges range in span from m = 4 to 8 and n = 2 to 6. For the majority of frameworks, structural studies using X-Ray diffraction show a chair-like shape in the solid phase. Weak X······X or weak C-H······π interactions are the origin of these formations. The synthetic route is shown in Scheme 12. Structural frameworks are shown in Figure 10. 5-DiyneS_2-2, 5-DiyneS_2-3, 7-DiyneS_2-5 and 5-DiyneSe_2-2 show columnar architectures. Gleiteret al.[16] further reported that a stepwise process could be used for generating cyclic tetraselenadiynes. α,ω-Diselenocyanatoalkanes (m = 2–5) and the Li-salt of trimethylsilylacetylene were involved in key steps. The resultant bis-Li-salt of α,ω-diselenaalkadiynes (m = 2-5) were treated with α,ω-diselenocyanatoalkanes (n = 2-5) again which gave rise to cyclic tetraselenadiynes having methylene chains of lengths m and n between the Se-C≡C-Se groups [Scheme 13]. The yields are quite low. We observe that rings having m = n, have the largest yields (35–45%). Secondary processes which produced byproducts with identical chain lengths, as illustrated in Scheme 14, constituted one cause of the reduced yields in instances of rings with variable lengths of the chain between the Se-C≡C-Se building blocks. In the solid state, the architectures of seven ring networks were studied [Figure 11]. Such studies show that the rigid Se-C≡C-Se components, which attempt to follow the torsion angles associated with CH_2-Se σ-bonds within 60°-90°, are what dictate the molecular architectures. Both the systems 5- DiyneSe$_4$-3 as well as 5- DiyneSe$_4$-5 exhibit columnar formations in crystalline state, which are likely attributed to strong interactions between Se atoms of nearby rings. Through combining the appropriate open chain dithia-α,ω-diynes, cyclic bis(1,3-butadiynes) with sulphur centres located in the α-position to the 1,3-butadiyne molecules were produced. In another method, Gleiter et al.[17]used dilithium-1,3-butadiynide to interact with α,ω-dithiocyanatoalkanes or α,ω-diselenocyanatoalkanes to generate a four-component cyclization [Scheme 15]. The cyclic dimers or trimmers were both possible with this notion. In the solid state, the majority of the cyclic dimer and trimer of sulphur molecules assume chair-like shapes. For cyclic dimer of Sulfur when n = 5, cyclic trimer of Sulfur when n = 5, Cyclic dimer of Selenium when n = 4, and cyclic trimer of Selenium when n = 4, 5, all experienced tubular forms in their solid state having close proximity within the chalcogen centres of neighbouring stacking. Incorporation of the solvent molecules as guests was obtained upon recrystallization of the cyclic trimer of selenium when n = 5, using different nonpolar as well as polar environments [Figure 12]. According to calculations, the solvent-accessible proportion varied from 19% (for n-hexane) to 25% (for mesitylene). Methylene chains' flexibility and the readily adjustable torsional angles that connect the hard 1,3-butadiyne rods were what give these cycles their elasticity qualities.



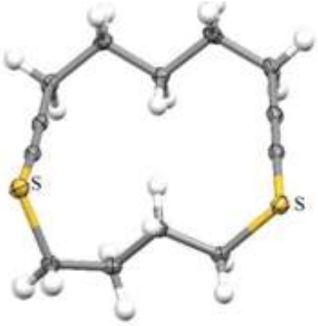
Scheme 12

4-DiyneS$_2$-3

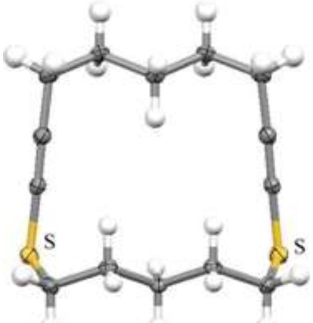


5- DiyneS$_2$-2

5-DiyneS$_2$-3



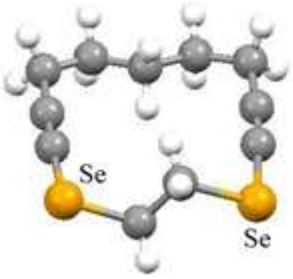
5-DiyneS_2-4



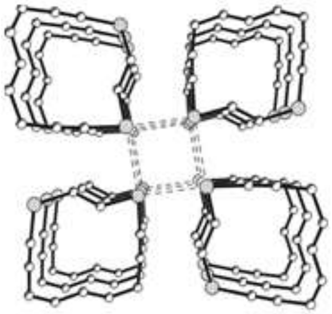
5-DiyneS_2-5

7-DiyneS_2-4

7-DiyneS_2-5

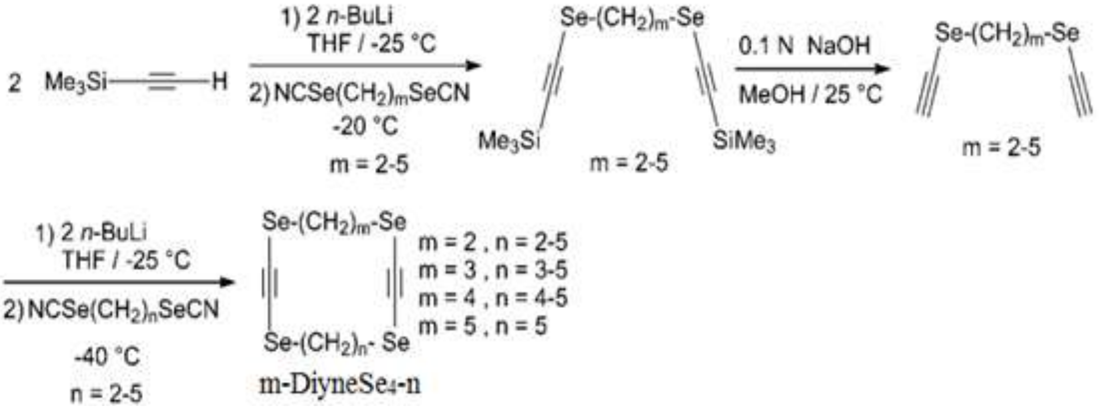


5-DiyneSe_2-2

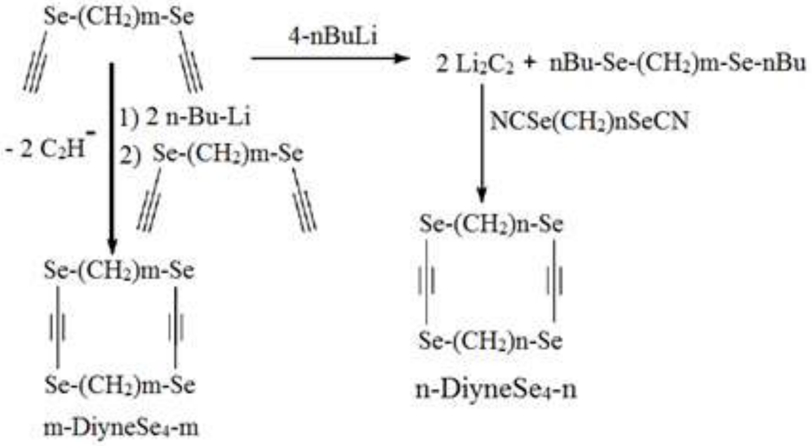


Tubular structure of **5-DiyneS_2-2** in the solid state

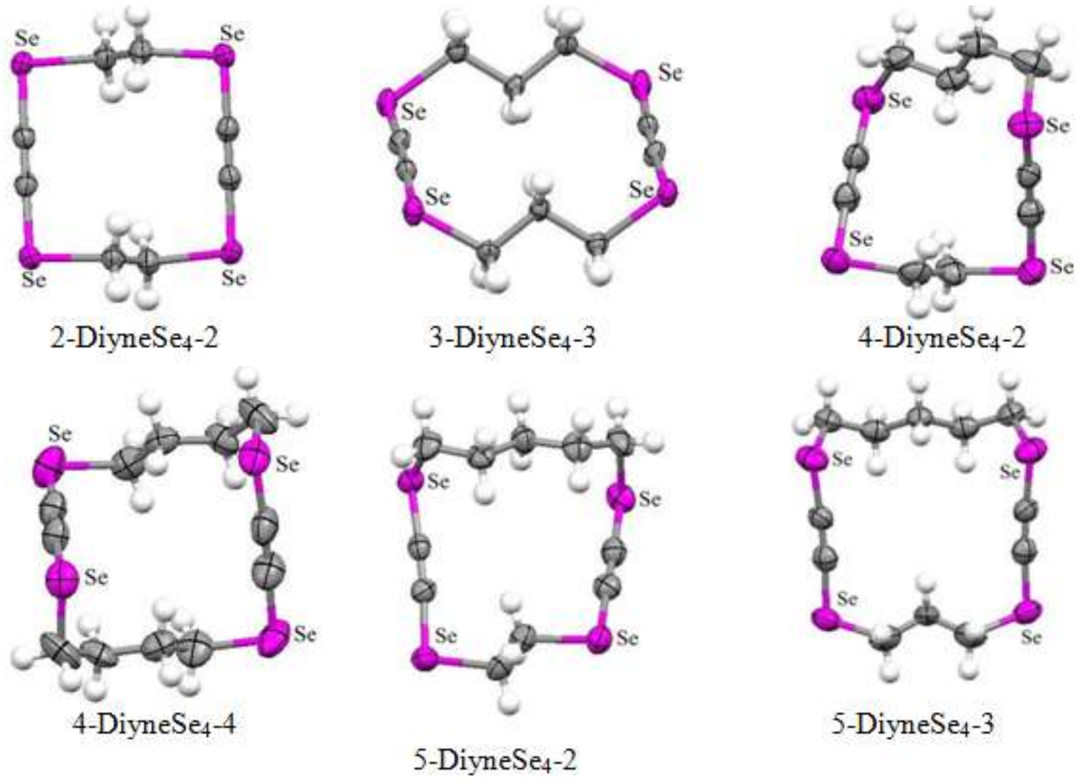
Figure 10



Scheme 13



Scheme 14



2-DiyneSe$_4$-2

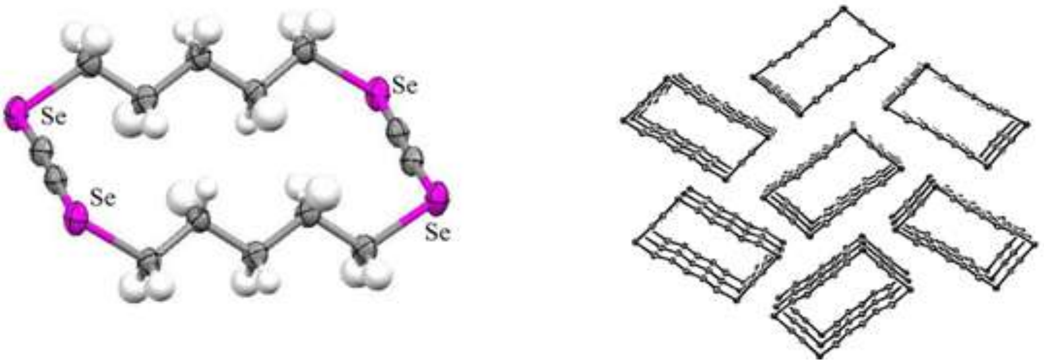
3-DiyneSe$_4$-3

4-DiyneSe$_4$-2

4-DiyneSe$_4$-4

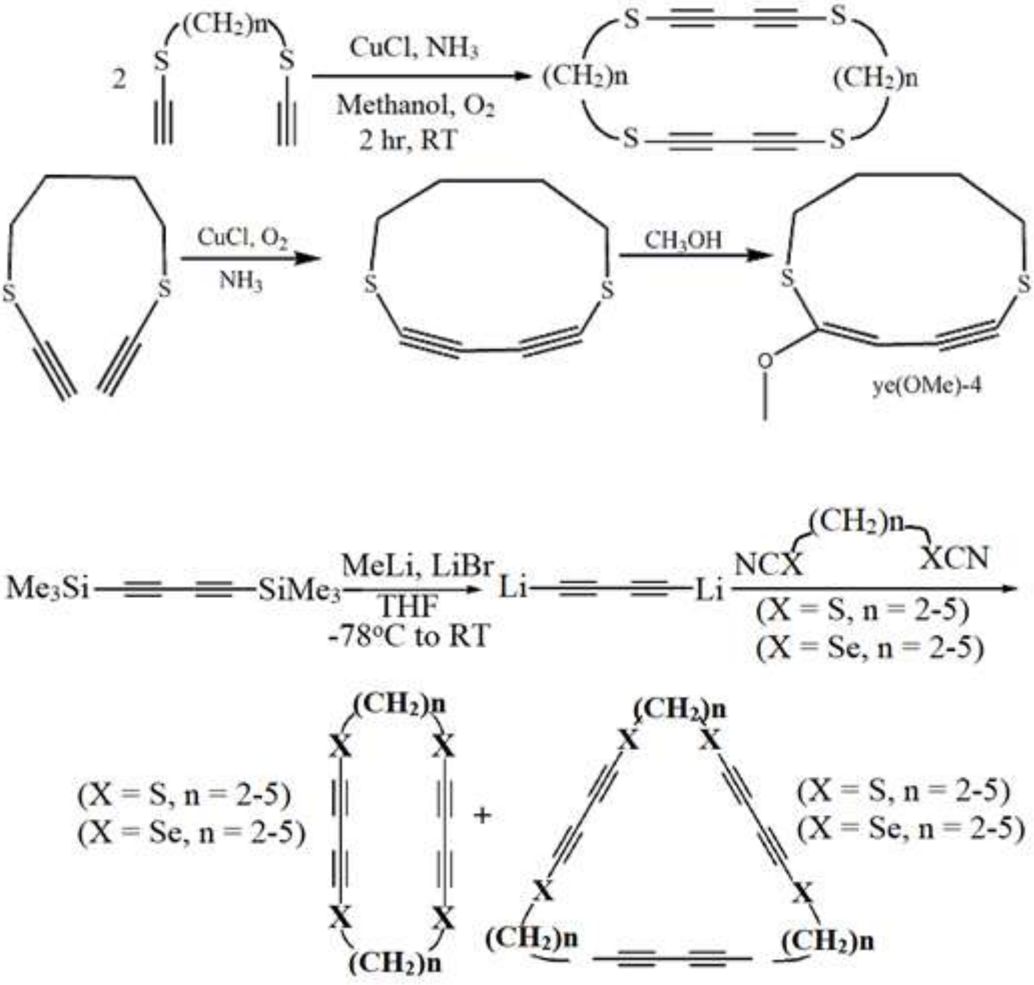
5-DiyneSe$_4$-2

5-DiyneSe$_4$-3



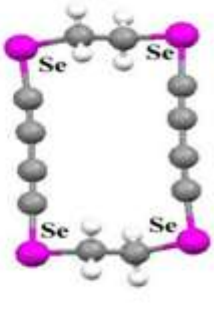
5-DiyneSe$_4$-5 and Columnar structures of 5-DiyneSe$_4$-5 in the solid state

Figure 11



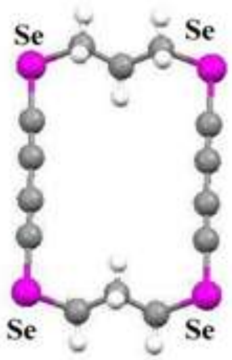
Scheme 15

2-TetrayneS$_4$-2

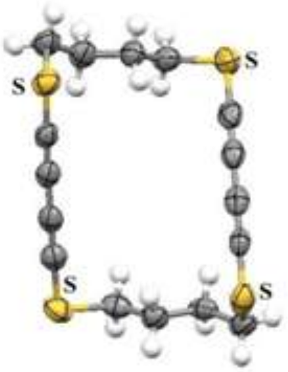


2-TetrayneSe$_4$-2

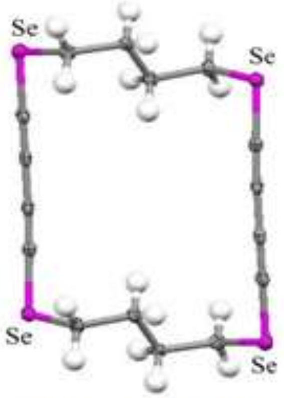
3-TetrayneS$_4$-3



3-TetrayneSe$_4$-3

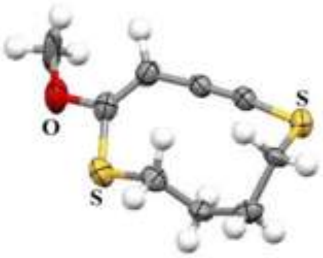


4-TetrayneS$_4$-4

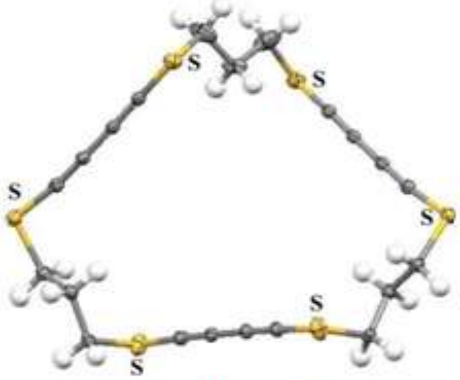


4-TetrayneSe$_4$-4

5-TetrayneS$_4$-5

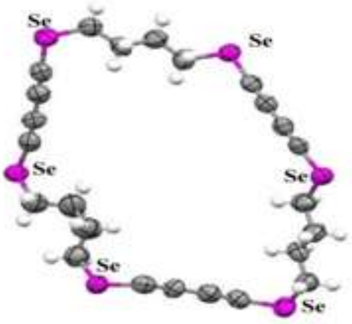


Yne-ene(OMe)S$_2$-4



3,3,3-HexayneS$_6$

4,4,4-HexayneS$_6$



4,4,4-HexayneSe$_6$

5,5,5-HexayneSe$_6$

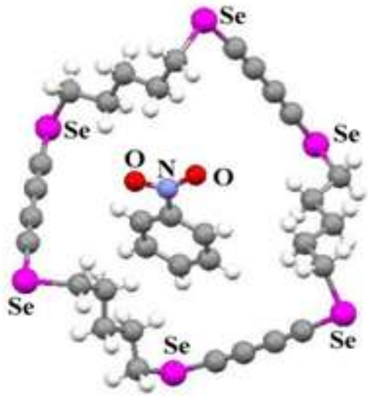
5,5,5-HexayneSe$_6$ with included 4-Bromo Anisole

5,5,5-HexayneSe$_6$ with included Anisole

5,5,5-HexayneSe$_6$ with included Benzene

5,5,5-HexayneSe$_6$ with included Chlorobenzene

5,5,5- HexayneSe$_6$ with included Mesitylene

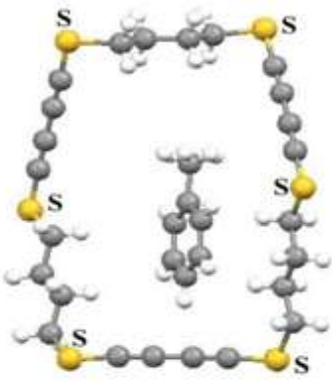


5,5,5-HexayneSe$_6$ with included Nitrobenzene

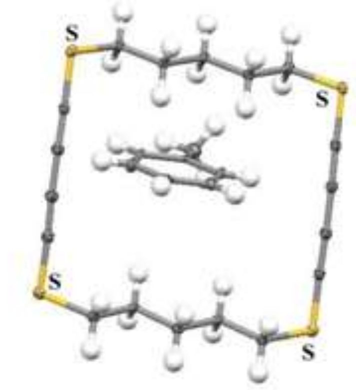
5,5,5-HexayneSe$_6$ with included p-Xylene

5,5,5-HexayneSe$_6$ with included Toluene

5,5,5-HexayneS$_6$ with included Toluene



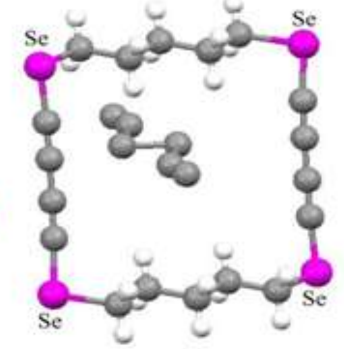
4,4,4-HexayneS$_6$ with included Toluene



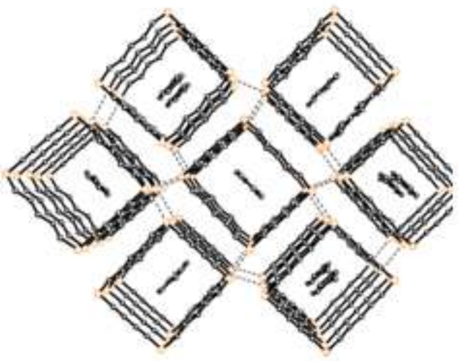
5-TetrayneS$_4$-5 with included toluene

5,5,5-HexayneSe$_6$ with included Aniline

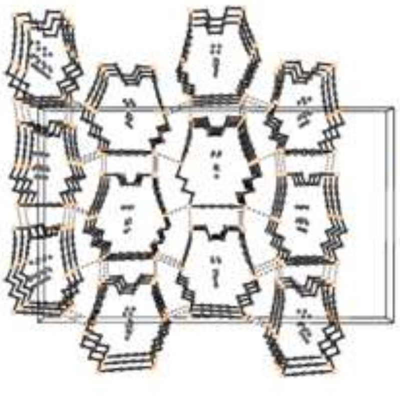
4,4,4-HexayneSe$_6$ with included Toluene



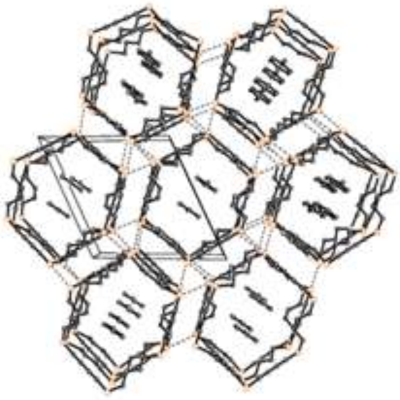
5, 5, 5-HexayneSe$_6$ with included n-Hexane



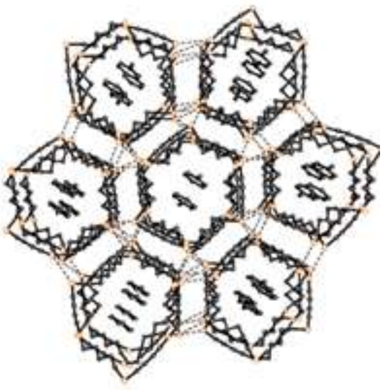
Columnar structure of 5-TetrayneS$_4$-5 in the solid state with included toluene



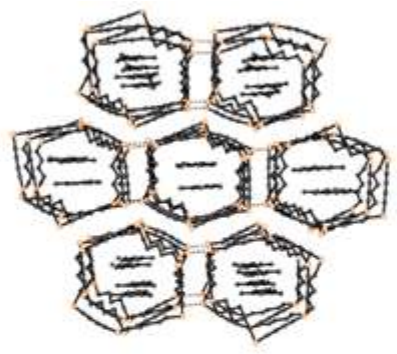
Columnar structure of 4,4,4-HexayneSe$_6$ in the solid state with included n-Hexane



Columnar structure of 4,4,4-HexayneSe$_6$ in the solid state with included Toluene



Columnar structure of 5,5,5-HexayneSe$_6$ in the solid state with included Toluene



Columnar structure of 5,5,5-HexayneSe$_6$ in the solid state with included Mesitylene

Figure 12

IV. CONCLUSION

Over the years researchers have investigated rigorously on the chemistry of chalcogen macrocycles. In this chapter, chemistry of unsaturated all sulfer and all selenium based macrocycles have been discussed briefly, mainly focusing on their synthetic and metal complexation as well as structural details which generated column-like architectures easily due to secondary interactions.

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