**Chemistry of Some Interesting Selenium-Nitrogen Containing Mixed Donor Macrocycles; Synthesis and Structural Viewpoints**

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**Abstract:**

Since the development of thia-crown ethers and their vast coordination chemistry and practical applications in numerous fields, scientists have shown huge interest in analogeous selena-macrocycles. Due to its “soft” nature, all selena donors containing macrocycles with multiple Se donors and variable core diameter has been synthesized and investigated. However over the years, there have been attempts to include hard or moderately soft other hetero donor atoms. This presence of hard as well as soft donor centers in a single ligand framework enables the ring to bind a wide range of metal ions, leading to not only intriguing coordination chemistry but also a large range of potential practical applications. In this chapter selena-macrocycles possessing hard nitrogen donor atoms are highlighted. Selena-aza crown ethers, selena-aza schiff base-corwn ethers, selena-aza cryptands, macrocycles containing protonated polyammonium groups and their chemistry have been discussed, from their synthetic and structural viewpoints.

**Introduction**:

Since the groundbreaking find made by Pedersen1, Cram2, and Lehn3, the field of "supramolecular chemistry" or "host-guest chemistry" has advanced tremendously. Supramolecular chemistry includes, but is not limited to, the chemistry of molecules with a highly structured architecture or the chemistry that extends beyond conventional covalent bonding. The internal structure of the adducts is controlled by a multitude of relatively weak forces, which includes as H-bonding,  stacking, ion-dipole, dipole-dipole forces, van der Waals interactions, etc. Merely a handful of the many applications utilising exclusive interaction with metal ions include chemical sensing, the precise extraction of radioactive or poisonous metal ions from waste streams, membrane transport, the immobilisation of radioisotopes, phase-transfer catalysis, and other uses. Additional important areas include the development of (metallo)enzyme prototyping systems, activating small molecules, the precise interactions of anions, and the nucleophilic parts of neutral substances. Mixed donor macrocycles attracted a lot of interest because of having incredibly specialised capacity for binding/chelating metal ions. The insertion of a large Se donor atom should change the size of the ring's diameter and enable some novel coordination behaviour. Due to Se's low electronegativity, macrocycles comprising Se also behaves as effective ligands for bonding to transition metals, and this topic has received extensive research. As a result, macrocycles containing hard donor elements such, N, or O in their ring structure may serve as potential hetero dinuclear macrocyclic ligands. These macrocyclic ligands will have neighbouring 'hard' and 'soft' binding spots, enabling them to interact with both 'hard' and 'soft' guest ions and/or molecules. Alkali and alkaline earth metal ions possessing weak polarizability are referred to as "hard". Transition metal ions are commonly mentioned as "soft" cations because they are very simple to polarise. Whenever a hard cation along with a soft transition-metal cation combine together to produce complexes, both staying inside the same macrocycle, the redox properties displayed by the transition-metal cations will vary. These substances can be used for bimetallic catalysis4, molecular activation as well as the building supramolecular networks. This chapter briefly discusses selena-macrocyclic ligands that also include hard nitrogen donor centers from their synthesis, metal complex formation, as well as structural perspectives.

**Selenium-Nitrogen donor atom containing macrocycles:**

Researchers studied novel selena-aza-crown ether; L1 and using its PtII compound catalysis of the hydrosilylation reaction of olefins by triethoxysilane were performed. PtII complex having L1: PtII = 2:3 (confirmed by elemental analysis) was synthesised and used as catalyst5. Synthesis of the ligand is shown in Scheme 1 and the catalysis reaction is shown in Scheme 2. There were also a number of selena-azacrown ethers (L2-L5) described by Hanseng et.al.6. The synthesis procedures are depicted in Scheme 3.

Using Scheme 4, the novel Se-aza-crown ether, L6, was produced. The analogous CuI and PtII compounds are produced when [Cu(H2O)6](ClO4)2 and [PtCl4] are reacted with L6, respectively. Even though CuII and PtIV were used during the first stages of the reaction, the production of CuI and PtII compounds {[CuI(L6)](ClO4)},{[PtII(Ring-contracted-L6)Cl2]} could be the result of the electron-transfer mechanism from Se atoms into the coordinating metal sites7. The complexation methods are shown in Scheme 5. The interaction of CuI through four Se atoms resulting in a distorted-tetrahedral configuration without  interactions among the surrounding complex components is visible in the crystalline form of the CuI compound. Switching the core CuI ion into a PtII ion to create a ring shrunk compound that reduces a 20-membered ring to a 10-membered ring. Two Se atoms and two Cl- connect the PtII core, completing a square planar architecture without any contact among PtII and nitrogen. The PtII compound's packing architecture reveals a variety of connections between the compound's monomers. The structures are displayed in Figure 1.

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| Scheme 1 |
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| Scheme 3 | |
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| Scheme 5 | |
| Cation of [Cu(L6)](ClO4)C:\Users\PARTHA\Desktop\[Cu(L26)](ClO4).jpg | [Pt(Ring-contracted-L6)Cl2]C:\Users\PARTHA\Desktop\[Pt(L26)Cl2].jpg |
| Figure 1 | |

In accordance with Scheme 6, an exclusive set of Se-macrocycles was produced through metal-free [2+2] condensing of bis(o-formylphenyl) selenide with a number of diamines8,9,10. It marked the first occasion where macrocyclic Schiff base had been found to contain Se. By minimising the unfavourable lone pair-lone pair interaction among the N atoms, secondary intramolecular Selenium-Nitrogen interaction provides a crucial part in the generation of the macrocycle and serves as a model towards the synthesis of the ring.

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| Scheme 6 |

Secondary Se**……..**N connections may be seen in the frameworks of all macrocycles, with the 22-member L7 exhibiting the strongest interactions. The largest transannular Se**……**Se separation is found in L9. The molecules' crystalline shape suggests that each Se atom only has one attractive interaction. The cavity dimensions are significantly altered [L15] by substituting a cyclohexane bridging for an ethylene link. The corresponding compounds are produced when L7 or L9 react with [PdCl2(COD)] (COD = 1,5-cyclooctadiene) in refluxing CH3OH, as indicated in Scheme 7. Figure of L7, L9, L11, L15 and PdII complex of L7 are shown in Figure 2.

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| Scheme 7 |

The crystalline architecture for the compound supports the microanalytical as well as spectroscopic findings that demonstrate the hydrolysis of two -CH=N of the macrocycle (L7) to -CHO groups8. This hydrolysis might be driven by high ring stress that pushes the metal to assume a planar shape. Instead cationic complex [Pd(L)]2+ [L = macrocycle formed by bis(o-formylphenyl) telluride and 1,2-diaminoethane]11 is produced by an equivalent interaction between the PdII precursor and the 22-member Te analogue with no  hydrolysis12. This could be explained by the Te analog's greater diameter of cavity (Te**.....**Te 4.979 Å). Via N2Se2 interaction, the structure surrounding PdII is square planar. The Se atom and O atom have a moderate interaction (2.855 Å). The microanalytical as well as spectroscopic information provided confirmation of the composition and geometry of [Pd(L9)](PF6)2.  L9's huge ring diameter (24 member; Se…..Se distance 7.229 Å) likely prevent Se atoms from being coordinated to PdII.

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| Scheme 8 |

The corresponding paramagnetic metallic compounds are produced when MX2.6H2O [M= NiII, X= Cl or CoII, X= Cl/ClO4] is reacted with L7, L9, or L15 (Scheme 8). Distorted octahedral geometry is completed by the NiII ion inside, which is bound to all four N and two Se donors. Two Se atoms are always mutually *cis-* to one another. The NiII compound and the corresponding CoII complexe of L9 are isostructural. Unexpectedly, the CoII compounds of L7 as well as L15 have low-spin, while the combination for L9 is high-spin8,10. Crystal structures of [Ni(L7)](PF6)2, [Ni(L9)](PF6)2, [Ni(L15)](PF6)2 and [Co(L9)](ClO4)2 are displayed in Figure 2. When exposed to metal salts, such Schiff base macrocycles become vulnerable to hydrolysis as well as transmetallation, resulting in macrocycle fragmentation. Therefore, reduction of each of the macrocycles (L7, L9, L11, and L15) was carried out in order to produce the amino counterparts that are higher in chemical stability as well as flexibility compared to their Schiff base ancestors8,9,10. This was done in order to analyse the binding behaviour of the reduced version of the Schiff base macrocycles. Additionally, compared to the original Schiff base macrocycles that consist of sp2 hybridised donor atoms, the reduced version of macrocycles just consist of sp3 hybridised donor atoms, as a consequence are capable of supporting a broader variety of shapes and sizes.

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| L7 | L9 |
| C:\Users\PARTHA\Desktop\L31.jpgL11 | C:\Users\PARTHA\Desktop\L35.jpgL15 |
| C:\Users\PARTHA\Desktop\[Pd(L27)](PF6)2.jpg | C:\Users\PARTHA\Desktop\[Ni(L27)](PF6)2.jpg |
| Cation of PdII complex of modified-L7 | Cation of [Ni(L7)](PF6)2 |
| C:\Users\PARTHA\Desktop\[Ni(L29)](PF6)2.jpg | C:\Users\PARTHA\Desktop\[Ni(L35)](PF6)2.jpg |
| Cation of [Ni(L9)](PF6)2 | Cation of [Ni(L15)](PF6)2 |
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| Cation of [Co(L9)](ClO4)2 | L8 |
| Figure 2 | |

The multinuclear NMR spectra as well as single crystal X-Ray architectures of the macrocycles show decreased Se**…..**N interactions in the reduced versions. Only one among the two potential N donors accessible for interacting with the Se atom interacts with it, as shown by the molecular framework of L8 (Figure 2). The greater cavity diameter compared to its corresponding Schiff base L7 is indicated by the increased Se**……**N as well as Se**…...**Se lengths, respectively. Researchers investigated their metal complex formation reactions using different transition metal ions. The NiII compound [Ni(L8)](PF6)2 has an architecture13 that is comparable to [Ni(L7)](PF6)2. For the distorted octahedral configuration, the two Se donors exist *cis-* to one another just as the case is in the original Schiff base compound [Ni(L7)](PF6)2. The synthesis of the hydrolyzed compound8 with L7, as indicated in Scheme 7, is in contrast with the generation of specified 1:1 compounds13 [Pd(L8)](PF6)2 and [Pd(L8)]Cl2 via the interaction of PdII salts with L8 [Scheme 9]. This might be because L8's diameter of the cavity is greater than L7's. A likelihood of Se binding with the metal in solution Phase, that does not appear in the crystal framework, is suggested by the downfield shift of the peaks of [Pd(L8)](PF6)2 as well as [Pd(L8)]Cl2 from 77Se NMR spectroscopy ( = 869 and 787 ppm, respectively). The 1H NMR spectroscopic investigation of [Pd(L8)](PF6)2 at different temperatures (20–120°C) in dimethylsulfoxide solution demonstrates the fact that the coalescence of the spectra might be caused by the compound's fluxional behaviour in solution phase. The sole fluxional mechanism that successfully makes the metal hop across the macrocycle's all six donor regions is the one that delivers this outcome [Scheme 10]. They are isostructural, both compounds. In its crystal structure, Pd2+ assumes a square planar shape involving linkage around its four N donors (Figure 3). In contrast, softer donor sites Se/Te bind to PdII for compounds of mixed donor Se/Te macrocycles comprising Oxygen or Phosphorus14,15,16,17. This unusual behaviour is caused by the chelate effect as well as the geometrical requirements of the ligand surrounding the core PdII ion for interaction with donor atoms13.

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| Cation of [Pb2(L12)(OAc)2](PF6)2 | | Cation of [Co(L17)]Cl3 | | |
| Figure 3 | | | | |
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| Scheme 10 | | | | |

Similar interaction between PtCl2 and L8 result in metal complex with ligand modifications13,18. The PtIV compound of L8's architecture (Figure 3) strongly supports the development of an unanticipated 23-member metalla-macrocyclic compound containing a C-Pt-Se link. Octahedral structure surrounds PtIV. Due to the significant *trans-* effect of -SePh, the Pt-N bond *trans-* to Pt-Se is lengthier compared to the remaining two Pt-N bonds. Contrary to the published stable PtII and PtIV compounds containing homodonor as well as mixed donor cyclic Se-ether ligands, the behaviour of L8 that produces the PtIV compound by oxidative addition of the C-Se bond to the PtII core is different15,19,20,21. The considerably more polar C-Se bond resulting from the Nitrogen→Selenium intramolecular interaction that exists in the original macrocycle (L8) might have helped the easy oxidative addition for this instance. C-Se bond oxidative addition to PtII is quite uncommon. The stable behaviour of the cationic PtIV component that has a selenolate bonding at the macrocyclic ring is additional new aspect regarding this metalla-macrocycle. The 1:1 interaction13 of [Cu(CH3CN)4](ClO4) with L8, in the presence of NH4PF6 in methanol, produced the compound [Cu(L8)](PF6)2. The square planar shape of the compound is confirmed by EPR spectrum as well as the magnetic moment (1.79 BM). The analogous HgII compound [Hg(L8)](PF6)2's 77Se NMR spectra shows a single signal at  = 315 ppm (for L28;  = 55, 329 ppm), showing that Se and HgII have no interaction13 (Scheme 9). Using a 1:1 and 1:2 (ligand:metal) proportion, respectively, the compounds [Pd(L12)](PF6)2 and [Pd2(L12)](PF6)2Cl2 were produced by the interaction of  L12 with PdII precursors (Scheme 9). The inability to completely characterise [Pd2(L12)](PF6)2Cl2 was caused by its weak solubility. Via the coordination of N4 donors from the potential N6Se2 coordinating environment, the crystalline framework of [Pd(L12)](PF6)2 exhibits the square planar architecture13 of the cationic unit [Figure 3]. A mercurous cation is coordinated inside the macrocycle22 core of [Hg2(L12)](PF6)2. This is the very first and most uncommon instance of a structurally characterised HgI compound of a monocycle [Figure 3] having Hg22+ confined within the monocycle's cavity. Potential binding of the Se donors to Hg22+ in solution is ruled out by the insignificant difference between the peak locations of [Hg2(L12)](PF6)2 and L12 in 77Se NMR. Despite the anticipated soft-soft interaction among the Hg22+ ion and the Se donor atoms, it binds to six N atoms to generate four five-member rings where the configuration surrounding HgI is antiprismatic. Instead of the development of six-member chelate rings that would occur via coordination by Se, this phenomenon is ascribed to the generation of stable five-member chelate rings. The generation of the mercurous ion might be caused by the association of the impurity HgO with Hg0, and the interaction between HgII and Hg0 significantly favours Hg22+, according to Catalano et al23,24. The 77Se NMR analysis of the dinuclear Pb compound [Pb2(OCOCH3)2(L12)](PF6)2 demonstrates that there is no connection between Se and Pb, allowing the compound to maintain its solid state structure in solution also22. PbII coordinating by both S as well as N atoms is observable when analogous interaction with the azathia macrocycle happens25. Stereochemically active lone pair of Pb2+ causes the structure around each PbII to be distorted octahedron. A central four-member Pb2O2 ring is formed by the bridging O atoms, and the two PbII. As shown in Figure 3, each OAc- ion within the structural unit bridges between two metal ions by using one of its oxygen atoms and also acts as a chelating ligand towards one metal ion.

Additionally, cryptands with Se and N donor atoms have been reported. The large Se atom's inclusion ought to alter the dimensions of the cage cavity, allowing certain intriguing coordinating behaviour.   Nitro-capped cage L17 having N3Se3 donor set has been reported [Schme 6]. Its CoIII compound; [Co(L17)]Cl3, reveals that metal ion is enclosed inside N3Se3 cage26. Its crystal structure is shown in Figure 3. Using Cs+ ions as the template, the cryptand L14 was synthesised via [2+3] condensing from tris(2-aminoehyl)amine and bis(o-formylphenyl) selenide [Scheme 6]9.

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| Scheme 11 |

Polyamine macrocycles [e. g. L8, L12] can serve as receptors for anions, cations, and neutral compounds as well. They can be polyprotonated in solution to produce positively charged polyammonium cations, that can form adducts with a range of inorganic, organic, and physiologically significant anions [such as; halides, sulphate, bisulphate, perchlorate, biphosphate, trifluoroacetate, nitrate etc.]27 through electrostatic forces and hydrogen bonding. As shown in Scheme 11, several macrocyclic compounds with various counter anions have been produced. The anion adducts of the Se-aza macrocycles' 77Se NMR spectrum show the fact that the sulphate adduct L8 [{H4(L8)}(SO42-)2], exhibits a significant upfield shift (the variation of ~241 ppm) in peak position relative to L8, while other adducts exhibit only a slight change. Shorter interactions between SO42- and L8 in solid form as well as in the solution phase can account for this upfield shift in the case of the adduct [{H4(L8)}(SO42-)2]. Of all the anions investigated, L8 exhibits the highest affinity for binding for SO42-, based to the 77Se NMR chemical shift value and the binding constant determined via the NMR titration technique. L8 and L12 form notable H-bonded compounds when combined with anions which are located above and below the macrocycle architecture, according to their crystal structures. While every other adducts reveal the macrocycles having been completely protonated, the trifluoroacetate adduct of L8; [{H2(L8)}(CF3COO-)2] assumes the di-protonated version of the macrocycle. Both significant H-bonding and  stacking interactions among the adducts are visible for the packing diagram of [{H6(L12)}(ClO4)6]. The unit cell of the adduct [{H4(L8)}(Br-)4] is made up of two separate molecules having a lot of H-bonding amongst them. To accommodate individual atoms' different bonding patterns, the macrocyclic framework has an extremely puckered ellipsoid shape. Here, neither of the Br- ions is located within the macrocyclic cavity, while one is located above the macrocyclic plane and generates intramolecular H-bonds with NH2+ and one water molecule's hydrogen atom. Bifurcated H-bonds are there between one of the N atoms and two Br- ions, while the second N atom is H-bonded to one Br- and a water molecule. The anionic adducts are shown in Figure 4.

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| Packing diagram of [{H2(L12)}(CF3COO-)4] | |
| Figure 4 | |

**Conclusion**:

In a nutshell, the Schiff base Se-macrocyles are appropriate for binding to different transition metal ions but are vulnerable to hydrolysis as well as transmetalation when exposed to metal salts, causing the macrocycle to cleave. The Te analogue generates transmetalated end-products with PtII,12 and HgII,11 ions, while the Se-aza Schiff base macrocycle L7 produces a hydrolysis compound using the PdII ion8. These Se-aza macrocycles can be converted into more flexible form by reducing their Schiff base parts. With regard to various metal ions, these reduced Schiff base macrocycles exhibit intriguing coordination characteristics. The PdII compound of L8, which interacts via solely N atoms compared to the N2Te2 coordination that exists in the Te counterpart18, is of particular significance. Te and PdII are coordinated because Te has a higher -donor characteristic than Se, which causes soft-soft interactions and stabilises the six-member chelate ring. Additionally, the 28-member Se2N6 macrocycle L12 exhibits possibilities as a binuclear binding ligand. The structural requirements of the ligand surrounding the metal ions and the chelating ring effect are thought to be the primary factors responsible for the remarkable non-interaction involving Se donor and metal ions throughout all of the compounds of L12. Anion recognition is still one of the very significant categories to investigate, despite the fact that cation's recognition and binding has been studied in much more details over several decades. Most of the enzyme substrates are anionic in nature. The designing and production of receptors for particular anion binding have undergone a revolution in the last two decades because of the significance of anion recognition. In order to explore how protonated analogues interact with various anionic substrates, the protonation of the amino counterparts was thereafter performed.

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