**Chemistry of Macrocycles Containing Only Sulfur Donors; Some Noteworthy Results**

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**Abstract:**

Thia macrocycles show rich coordination chemistry, producing isolated as well as polymeric metallo-supramolecular frameworks. Thia-donor networks' attraction towards soft metal ions and their capacity to help stabilising uncommon oxidation states for some metals are what define the way they interact. It is seen that thioether sulphur employed in a flexible macrocyclic framework will adopt a combination of an *endo-* and an *exo-* positioning with regard to that macrocyclic cavity, providing the development of endocyclic as well as exocyclic metal complexes. Additionally, the existence of *exo-*oriented Sulfer-donors being desirable synthetically because it offers a way to create S-bridged frameworks, which frequently correlate with lesser prevalent (and occasionally novel) compounds like a variety of polymeric metal coordination networks. The adoption of these strategies has frequently led to an array of unique and uncommon metallo-structures, as described in this article.

**Introduction**:

Since the groundbreaking discoveries of Pedersen1, Lehn2, and Cram3, which involved the production of cation specific crown ethers, cryptands, and spherands, the design and manufacturing of macrocycles with very specific sensors for metal's cations is continuing to advance. The potential of macrocyclic ligands as selective metal-ion binding agents has been extensively studied. The cyclic structure of macrocycles, that includes an inbuilt receptor cavity as the metal bonding site, renders them suitable for this function. The macrocyclic ring's constrained conformational flexibility helps to fit the metal ion's steric (and electrical) needs according to the macrocycle's cavity dimensions. There are several uses for macrocycles, particularly in the sensing as well as separating of diverse materials4. The macrocycle effect5, which occurs when macrocyclic ligand compounds outperform their open-chain counterparts in terms of kinetic as well as thermodynamic stability, led to their adoption as reliable building blocks6 for the construction of supramolecular structures. The metal ion in the aforementioned situations often exhibits endo(in cavity) [Figure 1A] binding. There are currently a lot of instances of macrocyclic frameworks that show metal ion bonding exo [Figure 1B] to their macrocyclic cavities, albeit being less prevalent. A lesser number of endo/exo structures, including homo- and heteronuclear endo/exo frameworks, have been constructed using ring structures that concurrently exhibit both endo- and exocyclic coordination to produce final structures that specifically represent the existence of dual coordination types [Figure 1C and 1D]. Exo-coordination is frequently, but not exclusively, connected with macrocycles that include thioether7. Numerous researches are being done on macrocycles with O, S, Se, and Te, as donating atoms. O, S- containing macrocyces are most common. Over the years, macrocycles with both mixed hard and soft donor atoms have found significance because they have the ability to bind two metals with different properties and oxidation states together in a single cavity. In this chapter, chemistry of macrocyclic ligands incorporating mainly all sulfur donor atoms is discussed categorically.

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| C:\Users\Hp\Desktop\Fig 1.gif  Figure 1 |

**All sulfur macrocycles and their metal complexes**:

With 1,4,7 trithiacyclononane (L1) and 1,4,7,10-tetrathiacyclododecane (L4)8; [Cd(L)2]X2 type of bi-ligand CdII complexes have been synthesized. Both L1 ligands interact facially in [Cd(L1)2](PF6)2 [Figure 3a] to form an architectural configuration with distorted octahedral coordination shape. In [Cd(L4)2](ClO4)2 [Figure 3b], each L4 connects to its four sulphur atoms, resulting in a unique S8 distorted square anti-prismatic coordination structure that resembles a sandwich. Numerous such ligands are reported in literature. Few of them are shown in Figure 2. Similar such compounds were reported, Such as, [Hg(L6)](ClO4)2, [Cd(L6)](ClO4)2, [Hg(L6)Cl2] etc.

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| Figure 2 |

L1 produces square planar compound, *cis*-[Pd(L1)Cl2]9 [Figure 4a], indicating the propensity of PdII to generate square-planar compound with a combination of neutral ligand and halides. Just two among three available S donors of L1 are bonded, as can be seen in the structure. The last S atom nevertheless is placed at the axial Pd-S distant connection proximity of 3.16 Ao over the PdS2Cl2 coordination plane. Additionally, the PdII core is 3.53 Ao away from one thioether donor of a nearby compound.

Such Ligands are synthesized by a generalized procure of reaction between appropriate thiol precursor and dibromo alkane in DMF under nitrogen atmosphere. Generally mixture of ligands are produced which are then purified by chromatographic separation. One such scheme of reaction in shown in Scheme 1, below10:

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| Scheme 1 |

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| Figure 3 | | | |

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| (b) | E:\Partha Pratim Das_27-07-2023\Book Chapter\New Projects\S,Se, Te macrocycles\Chem Draw\s3pdc8_1.jpg |
| Figure 4 | |

An X-Ray analysis of the structural framework of *cis*-[Pd(L1)Cl2] at different pressures revealed that, at 4.4 GPa, an abrupt shift from the mononuclear square planar framework to a zigzag chain polymer [Figure 4b] took place, along with a significant conformational modification to a portion of the bound macrocycle's backbone. Each PdII centre has a pseudo-octahedral architecture as a result of the contraction of the in-plane Pd-S and above-plane Pd-S lengths to 2.85 and 3.12 Ao, respectively. The transition is reversible when the pressure is reduced.

In the framework of [Pt(L1)(tmphen)](PF6) [Figure 5], the compound assumes a *cis*-square-planar setup, with the bidentate tmphen ligand occupying two slots of the square and the thioether donors from L1 filling the other two. These Pt-S bond lengths at 2.27 and 2.26 Ao, respectively, are not exceptional. A lengthy connection of 2.88 Ao, develops to the Platinum (II) core due to the third macrocyclic thioether atom's intriguing placement above the square plane, giving the Pt centre a pseudo-5-coordination, distorted square pyramidal shape generally.

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| Figure 5 |

Numerous mixed-ligand PdII and PtII compounds of the type [ML(L1)](PF6), where M is either palladium(II) or platinum(II); L is either ppy (2-phenyl pyridine) [Figure 6a], bzq (7,8-benzoquinolinate) [Figure 6b, 6c], or {CH2C6H4P(o-tolyl)2} [Figure 6d, 6e], have been described11. Compounds with cyclometallation were isolated for every instance. Figure 6 shows representative architectures of cations of all such products. In each complex, L1 once more forms a planar coordination between two thioether-donors and two donor atoms from the respective co-ligand.

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| Figure 6 | | | | | |

The axial M-S distance for all complexes is likewise greater than would be predicted for a typical metal-coordinate bonding, but it is still shorter than the total of the individual van der Waals radii. The structural framework of L1 is disordered, providing the formation of two distinct types; exo-S-axial and endo-S-axial [Figure 6c], having exo-form constituting the predominant constituent. Investigations reveal that in these compounds the metal-bound L1 ligand displays fluxional activity in CD3NO2, as has been seen for similar species.

Additionally, PtII compounds of L1 with two XPh3 (X = As or Sb) co-ligands as well as the similar compound [Pt(L1)(dpae)](PF6)2 [dpae = 1,2-bis(diphenylarsenio)ethane] were also produced. The following complexes are reported12: [Pt(L1)(AsPh3)2](PF6)2 [Figure 7a], [Pt(L1)(AsPh3)(Cl)](PF6) [Figure 7c], [Pt(L1)(SbPh3)2](PF6)2 [Figure 7b], [Pt(L1)(SbPh3)(Cl)](PF6) [Figure 7d], [Pt(L1)(dpae)](PF6)2 [Figure 7f], and [Pd(L1)(dpae)](PF6)2 [Figure 7e]. In all of those, the framework reveals that two S atom from L1 are once more attached to the corresponding metal centres in a square planar configuration, jointly with two XPh3 or the (bidentate) dpae ligand, with the third S atom from L1 holding an axial location. In Figure 7, the structures are displayed. In an additional investigation, it was shown that recrystallizing [Pt(L1)(SbPh3)3](PF6)2 from nitromethane at room temperature results in the sudden production of [Pt(L1)(SbPh3)(C6H5)](PF6)13 [Figure 7g].

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| Figure 7 | | | |

In the self-assembling process of a tetra PtII molecular square, [Pt(L1)(bipy)]4(OTf)8, containing bipy (4,4-bipyridine) edges, it has been observed that four L1 ligands are used as corner "capping" components14. Each L1 ligand displays fluxional habits in solution. This is true for all "formally" 4-coordinate corners PtII centres. Figure 8 depicts the solid state structure of cation. It has four triflate anions occupying the square's hollow. Later, it was demonstrated that even though the aforementioned square is stable in nitromethane, it gradually changes into a new complex that is probably the respective metallo-triangle in acetonitrile. Several more metal thia crown compounds were also described in the context of the aforementioned investigation. These comprised new PdII compound [{Pd(L1)Cl2}2(pyrazine)](OTf)2 [Figure 9d] and two RhIII complexes, cis-[Rh(L4)Cl2](PF6) [Figure 9b] and trans-[Rh(L5)(H2O)Cl](OTf)2 [Figure 9c]. Also identified was a hybrid platinum(II) complex of the type [Pt(L1)(CH3CN)2]2[Pt(L1)2](PF6)6 [Figure 9a]. These structures are shown in Figure 9. Only two S-donors are used by L1 to coordinate the aforementioned PdII and PtII complexes, respectively, whereas the third S occupies an axial position with a longer proximity to the corresponding metal ions (2.9 Ao for Pd and 3.0-3.1 Ao for Pt) 15.

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| Figure 8 |

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| Figure 9 | | | |

The [Ru(L1)(glycino)Cl] compound was synthesized by reacting [Ru(L1)(dmso)Cl2]16 (dmso = dimethylsulfoxide) [Figure 10] with a small excess of glycine in the presence of a base. This compound possesses an octahedral geometry due to the glycino ligand coordinate in its typical (O,N)-bidentate form)17. For 1:1 insertion in the cavity of cyclodextrin and similar substituted derivatives, this species serves as a guest.  Physical studies confirm the presence of bound glycinate is in the cyclodextrin cavity.

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| Figure 10 |

Electronic characteristics of bpta-bridged dinuclear compounds of the types [(RuL)2(bpta)](PF6)4 [Figure 11b and 11c], [bpta = 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine, L = L4 or L5], and [(RuL1Cl)2(bpta)](PF6)2 [Figure 11a] are affected by S-donor thiacrown ligands18. These complexes were made by reacting bpta to the respective parent [(Ru(S4-macrocycle)(dmso)Cl](PF6) compound; Figure 11 depicts the bridging architecture of the final products. It was proposed that the redox and electrical characteristics of each compound portray the bonding behavior of the S donors in the corresponding S4-crowns.

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| Figure 11 | |

Using two moderately labile co-ligands like Chloride, nitrate, water, or dimethyl sulfoxide, octahedral RuII compounds of the S4-donor, L4 and L6 ligands were produced19. The chemical composition of the compounds are *cis-*[Ru(L4)(dmso)(H2O)](CF3SO3)2 [Figure 12a], *cis-*[Ru(L4)(dmso)(ONO2)](NO3) [Figure 12b], [Ru(L4)2](CF3SO3)2 [Figure 12c], *cis-*[Ru(L6)Cl2] [Figure 12d], and *trans-*[Ru(L6)(dmso)(H2O)](CF3SO3)2 [Figure 12e]. The L4 ring is too small to wrap RuII, yielding only *cis-* complexes, whereas the bigger macrocycle generates both *cis-* and *trans-* octahedral species. The pyrazine's (pyz) reaction with the compounds revealed that the anion found in the precursor affects the type of substance that is later separated. The compound [Ru(L4)(dmso)Cl]Cl is *cis-*, pyz combines to form [(Ru(L4)Cl)2(pyz)]Cl2 [Figure 12f]. In a similar manner, pyz's interaction with cis-[Ru(L4)(dmso)(ONO2)](NO3), produces the dinuclear compound [Ru(L4)(ONO2)]2(pyz)](NO3)2. While *cis-*[Ru(L4)(dmso)(H2O)](CF3SO3)2 generates the analogous bridging trinuclear compound [{cis-Ru(L4) (pyz)}3](CF3SO3)6 [Figure 12g].

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| Figure 12 | | | |

Both [Ru(L4)(bpy)Cl]Cl [Figure 13a] and [{Ru(L4)Cl)2(bpy)](PF6)2 [Figure 13b] (bpy = 4,4-bipyridine), constitute mixed ligand compounds20. The RuII centres assume a distorted cis-octahedral coordinating architecture in each compound, binding to one N from bpy and chloride in addition to the S4-donor set of L4. Bypridine serves as a connector among the metal centers in the second compound. The electrochemical findings in each situation support the existence of the RuII/RuIII couple's reversible one electron mechanism. Creutz-Taube ion analogues21 were prepared as nine fresh compounds that include pairs of [RuII(L)Cl]+ components (L = L4, L5, or L6) connected by linear bis-monodentate linking N-donor ligands, pyrazine, 4,4-bipyridine, or 3,6-bis(4-pyridyl)-1,2,4,5-tetrazine. The coordinated S4-macrocycle's different ring sizes greatly affect the electronic delocalization throughout this set, although the RuII centres being linked to identical donor groups, according to the analysis of the inter valence charge transfer absorption patterns for the various compounds22. The [Ru(L7)Cl](PF6)23 [Figure 14] architecture reveals that the cation has a deformed octahedral framework, with the chloride unit assuming the sixth/axial site and all five S-donors of L7 linked in a square pyramidal way. Once more, this combination exhibits the RuII/RuIII couple's one electron redox activity in CH3CN.

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| Figure 13 | |
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| Figure 14 | |

Numerous mixed-ligand RuII compounds of L1, L4 and L5 with two nicotinamide, isonicotinamide, or p-cyanobenzamide co-ligands; [Ru(L1)(nicotinamide)2Cl](PF6) [Figure 15a], [Ru(L1)(isonicotinamide)2Cl](PF6) [Figure 15b], [Ru(L4)(nicotinamide)2](PF6)2 [Figure 15c], [Ru(L4)(isonicotinamide)2 ](PF6)2, [Ru(L4)(p-cyanobenzamide)2](PF6)2, [Ru(L5)(nicotinamide)2](PF6)2 [Figure 15d], [Ru(L5)(isonicotinamide)2](PF6)2 and [Ru(L5)( p-cyanobenzamide)2](PF6)2 [Figure 15e], in order that every single unit has amide (-CONH2) functionalities that are positioned peripherally and are accessible for generating hydrogen bonds24. These serve as the foundation for the construction of H-bonded solids. X-Ray diffraction was used for analysing six of them. While two of these systems produce networks using amide-anion N H•••F H-bonds connecting the complex components, four of these compounds build networks using amide-amide N-H•••O H-bonds. Figure 16 represents the H-bonded networks. Along the series, a shift from 1D to 2D architecture was seen.

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| Figure 15 | | | |

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| Hydrogen-bonded double chain linking [Ru(L5)(nicotinamide)2]2+ cations in [Ru(L5)(nicotinamide)2](PF6)2 and its representation |
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| Hydrogen-bonded double chain linking [Ru(L4)(nicotinamide)2]2+ cations in [Ru(L4)(nicotinamide)2](PF6)2 and its representation |
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| Hydrogen-bonded layers containing solvent/anion-expanded amide tapes of [Ru(L1)(nicotinamide)2Cl](PF6) and its representation |
| C:\Users\PARTHA\Desktop\17.pngC:\Users\PARTHA\Desktop\18.png |
| Amide-Anion Hydrogen-Bonded Chain in [Ru(L5)( p-cyanobenzamide)2](PF6)2 and its representation |
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| 2D hydrogen-bonded structure of [Ru(L1)(isonicotinamide)2Cl](PF6) and its representation |
| Figure 16 |

Two of the S atoms are more likely to be preoriented endo- in relation to the macrocyclic cavity for every scenario when the maleonitride component is present in the L10 and L11 macrocycles25. Their crystal structures are shown in Figure 17a and 17b, respectively. The ligands are prepared by the procedure shown in Scheme 2. The following complexes were synthesized [Ag(L10)2]BF4 [Figure 17c], [Ag(L10)2](PF6), [Ag(L10)](BF4), [Ag(L10)](PF6), [Ag2(L10)3](BF4)2 [Ag(L11)2](BF4) [Figure 17d], [Ag(L11)2](PF6), [Ag(L11)](BF4), [Ag(L11)](PF6) and [Ag2(L11)3](PF6)2 [Figure 17e]. The bis-ligand combination [Ag(L10)2]+, which has a sandwich like  structure as well as S8-coordination (distorted cubic shape), is produced when the 12-membered L10 interacts with AgI salts. Conversely, an important modification in the coordination tendency with AgI occurs when the S4 macrocycle's ring dimension is increased to 13 atoms to produce L11. In this instance, the AgI complexes [Ag(L11)2]BF4 and [Ag2(L11)3](PF6) were separated. Producing distorted square pyramidal coordinating environment, the Ag(I) in [Ag(L11)]+ is attached to four S atoms from one L11 and one S from a second L11, functioning as a monodentate ligand. [Ag2(L11)3](PF6)2 cation is made up of two [Ag(L11)]+ components. In every component, the metal centre is coordinated with four S atoms of L11 type. A second L11 macrocycle that combines in a bis-monodentate fashion using cis-S atoms connects the metal centres in both units. This allows each AgI centre to attain 5-coordination and exhibit a distorted square pyramidal structure. The structures are shown in Figure 17.

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| Scheme 2 | | | |
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| (c) | C:\Users\PARTHA\Desktop\[Ag(L10)2]BF4.png | | |
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| Figure 17 | | | |

In an additional investigation, HgII was used to generate compounds containing L10 and L11. For instance, Hg(ClO4)2 interacts with L11 to produce a dinuclear compound [Hg2(L11)3] (ClO4)4, that has macrocycle bridges and shares structural similarities with the dinuclear AgI compound described previously26. Complexes of category HgX2L (X = Chloride or iodide and L = L10 or L11) were produced using HgII chloride and iodide. In the investigation, the equivalent 15-membered, S5 maleonitrile counterpart L12 was also synthesised. This ligand generates a 1:1 (metal: ligand) compound of type [Ag(L12)]X (X = ClO4- [Figure 18a] or BF4- [Figure 18b]) when combined with AgI.

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| Scheme 3 | | | |
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| Figure 18 | | | |

In every compound, the cation exhibits zigzag chain architecture. L12 was synthesized as in scheme 3. The following compounds [Figure 18] are reported; [Ag(L12)]ClO4 [Figure 18a], [Ag(L12)]BF4 [Figure 18b], [Hg2(L11)3](ClO4)4 [Figure 18c], [HgCl2(L10)] [Figure 18d], [HgI2(L10)] [Figure 18e], [HgCl2(L11)] [Figure 18f], [HgI2(L11)2] [Figure 18g] and [PtCl2(L10)] [Figure 18h].

In an additional investigation, it was shown that the S5-donor macrocycle L7 can interact with CrIII to create a deformed octahedral compound [Cr(L7)Cl3]27 [Figure 18i] where this ligand binds facially by three of its S-donors, while the rest coordination sites filled by three chloride ligands. Two L7 S-donors continue to be acting non-coordinated.

As potential equivalents of the "blue" copper proteins, 21-membered S6-donor ligand L13's [Figure 19a] CuI/CuII compounds was studied28. The flexible nature of this macrocycle was thought to have contributed to the development of an adequate tetrahedral configuration for CuI, which is why this macrocycle was found to prefer coupling to CuI over CuII by a margin of twelve orders of scale. The CuI complex's [Cu(L13](ClO4) [Figure 19b] solid state framework reveals that four S donors of L13 bind in a distorted tetrahedral configuration around the CuI centre, while the other two donors in the surrounding ring are unbound. Thiamacrocycles have the unique capacity to stabilise particular metals at their lower oxidation states29.

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| (c) | C:\Users\PARTHA\Desktop\35.png | (d) | C:\Users\PARTHA\Desktop\AgIIS6_150K.jpg |
| Figure 20 | | | |

In the X-Ray structures of cations of the complexes [Au(L1)2]1+/2+/3+, the binding of AuI, AuII, and AuIII centres [Figure 20a, 20b and 20c, respectively] have been described30,31. Thorough analysis of [AuII(L1)2](BF4)2 and [AgII(L8)](ClO4)2’s electronic characteristics were reported32 [Figure 20d]. Second compound was the first of this type of AgII entities to involve complete thioether donor binding and was structurally characterized. The distances between the different Ag-S bonds are smaller than they are in the similar AgI octahedral compound. Thioether donors serve a “non innocent” role in maintaining the theoretically +2 oxidation levels that these entities exhibit.

**Conclusion**:

Over the years, chemistry of only thioether containing macrocycles have developed to a great extent, credit goes to their vast, yet interesting coordination chemistry. In this chapter, several such ligands are discussed along with their reported metal complexes and brief discussion of their molecular structural frameworks have also been done both for transition as well as non-transition metal ions, briefly.

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