CHEMISTRY OF SOME FASCINATING HOMOLEPTIC MACROCYCLIC POLYTELLUROETHERS, TELLUROMETALLOMACROCYCLES AND TELLURAPORPHYRINS; SYNTHESIS AND STRUCTURAL PERSPECTIVES

Abstract

Since long back, organic chalcogen hypervalent compounds have garnered a lot of attention. The study of telluranes has attracted much less emphasis even though the structural along with theoretical properties of selenuranes as well as hypervalent sulfuranes have both been extensively investigated. Even pollytelluroether macromolecules are also not so large in number, which is definitely not expected given the better σ-character and lower electro negativity of Te compared to S/Se. The development of unique macrocycles with various core size and metal binding capacities has been facilitated by core-modified porphyrins, in which part of the four N donors are substituted by one or more Te. Te-containing 21- and 23-core modified porphyrins carry out several types of catalysis reactions. In this chapter, few interesting molecules from three different types of tellurmacrocycles, e.g. homopectic macrocyclic polytelluroethers, tellurometallomacrocycles and telluraporphyrins have been discussed briefly from their synthetic and structural viewpoints.

Keywords: Homoleptic Macrocycle

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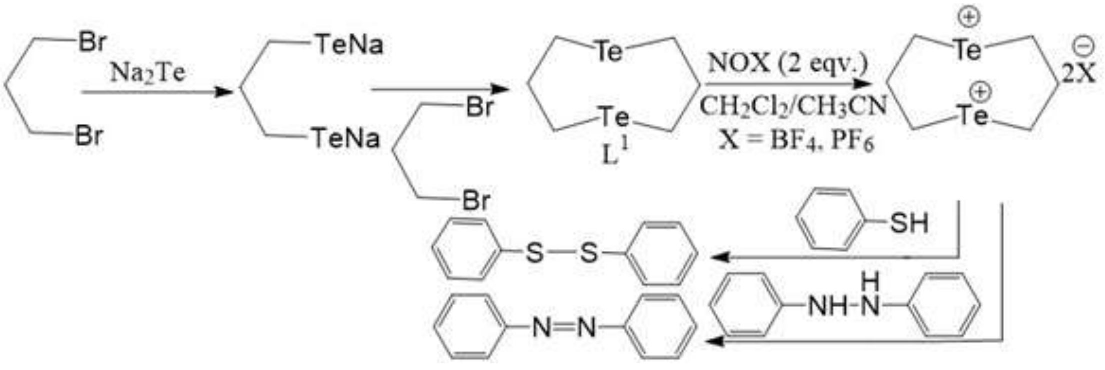
I. INTRODUCTION

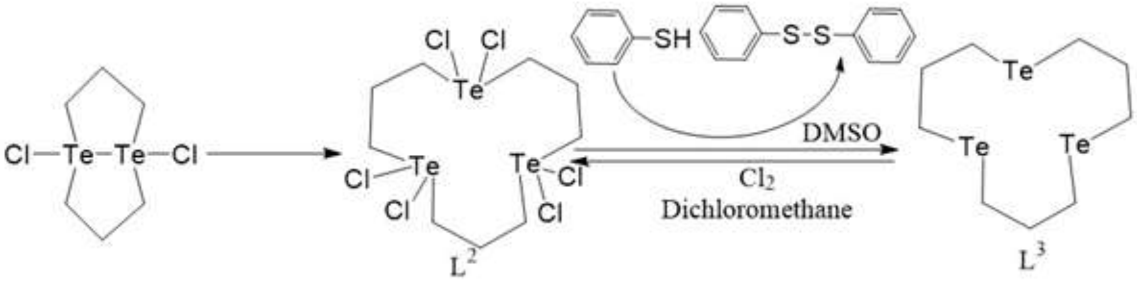
Over the past several decades, organic chalcogen hypervalent molecules have attracted a lot of interest. While the structural along with theoretical characteristics of selenuranes and hypervalent sulfuranes have been investigated in great detail, the chemistry of telluranes has received far less attention. Macrocyclic polytelluroether's crystal structure analysis is especially limited. Telluroether inclusion as donors (TeR_2) within a macrocyclic architecture should result in ligands susceptible to immeasurably extensive coordination chemistry due to Te's reduced electronegativity and consequently better σ-electron-donating characteristics in comparison to Se and/or S. Due to the accessibility of ^{125}Te NMR spectroscopy as a potent architectural probe, telluroether chemistry is much more appealing in these circumstances. Research on core-modified porphyrins, where some of the four N atoms are replaced by one or more heteroatoms O, S, Se, or Te, have led to the creation of novel macrocycles with different core dimensions as well as metal ion bonding capabilities. The intriguing category of compounds; Te-containing 21- and 21,23-core modified porphyrins operates catalysis for the activation of H_2O_2. In these substances, the 21-positioned Te atom is located opposite to NH or S at the 23-position and has taken the spot of one of the pyrrole N-H groups. By donating a lone pair of electrons, the heteroatom at position 23 can aid in the oxidation of the Te donor at position 21. When combined with H_2O_2 and NaBr, meso-Tetraphenyl-21-telluraporphyrins serve as catalysts towards bromination processes. In this chapter, some important macrocyclic homoleptic polytelluroethers, tellurometallomacrocycles and telluraporphyrins have been discussed in details from their synthetic and structural perspectives.

II. MACROCYCLIC POLYTELLUROETHERS (HOMOLEPTIC)

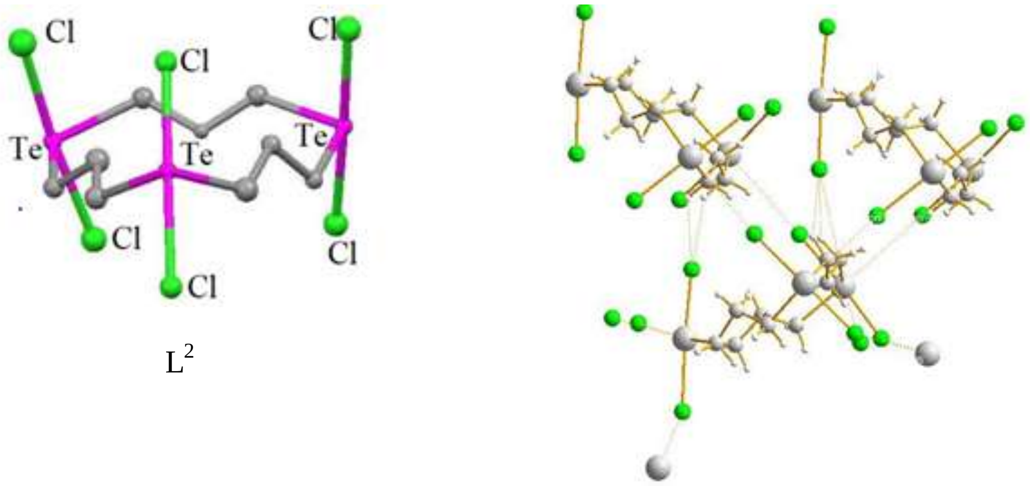
1,5-Ditelluracyclooctane (L^1), a unique eight-membered ring Te-macrocycle molecule, was reported[1] [Scheme 1]. The unusual ditelluridedication BF_4^- or PF_6^- salt, produced by two equivalents of $NOBF_4$ or $NOPF_6$ oxidizing the bis-telluride L^1, exhibits oxidizing properties. As an oxidant, the ditelluride dication salt functions as following [Scheme 1]. Diphenyl disulfide was produced in 91% yield when 2 equivalents of benzenethiol and 1 equivalent of the dication were treated in acetonitrile under an argon environment at room temperature for six hours. Similarly to this, when 1,2-diphenylhydrazine is treated with the dication and 1,4-diazabicyclo [2,2,2] octane (DABCO), 80% of the product is converted to azobenzene. Following the pyrolysis of an 8-member ring molecule, as described in Scheme 2, a novel chlorine derivative of a 12-member ring Te-macrocycle with three hypervalentTe^{IV} component [L^2] is published[2], which also serves as an oxidant. By creating Cl^- bridges between the molecules, this generates polymeric frameworks in the crystal structure. Similar to the majority of diorgano-Te^{IV} dihalides, topology around the metal center has been distorted trigonal bipyramid, with the two alkyl-C atoms and only lone pair occupying the trigonal plane's three ends and the more electronegative Cl^- occupying their typical axial sites [Figure 1]. The <Cl-Te-Cl along with <C-Te-Cl angles seem not to be much distorted by the lone pair of electrons, however the <C-Te-C angles have been brought into closer proximity by the increased volume of lone pairs.



Scheme 1



Scheme 2



L^2

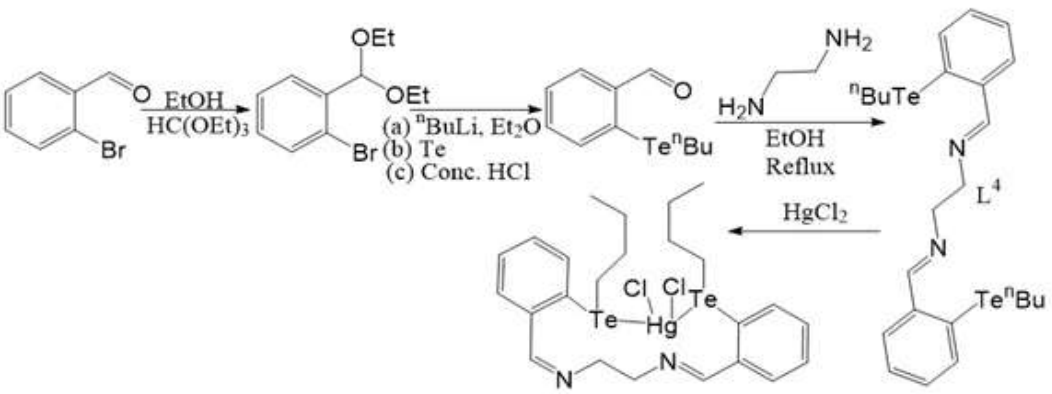
H-bonded network of L^2

Figure 1

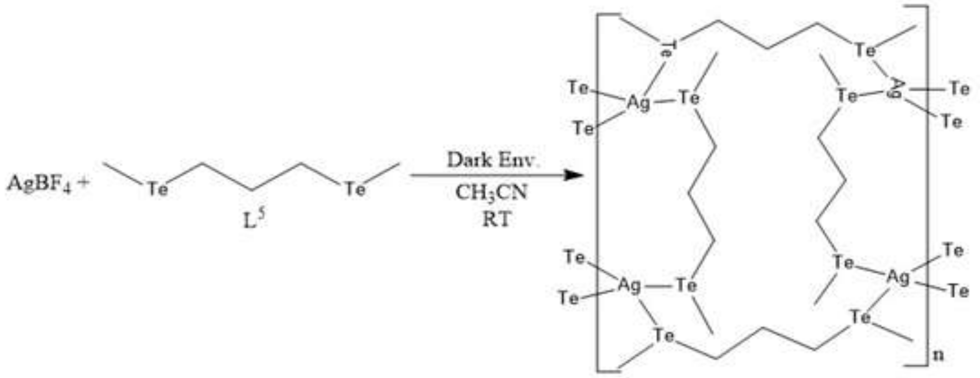
Te and Cl^- make several intermolecular interactions, which are typical of Te^{IV} complexes involving halogen-containing ligands, but there's no intramolecular connection between the Te atoms. Te^{IV} has a larger coordination number due to intermolecular interactions compared to what is anticipated by the molecule's stoichiometry. In the presence of Et_3N in DMSO under Argon atmosphere for 10 minutes at 50°C, 6 Equivalent Thiophenol interacted with one Equivalent of L^2 to produce a disulfide which had 90% yield as the oxidation product along with neutral L^3 with a 90% yield as the reduction product, as illustrated in Scheme 2. This's noteworthy to note that L^3 produces L^2 in a good yield when it interacts with Cl_2 in dichloromethane at room temperature.

III. TE-MACROCYCLIC CHELATES/ TE-METALLOMACROCYCLES

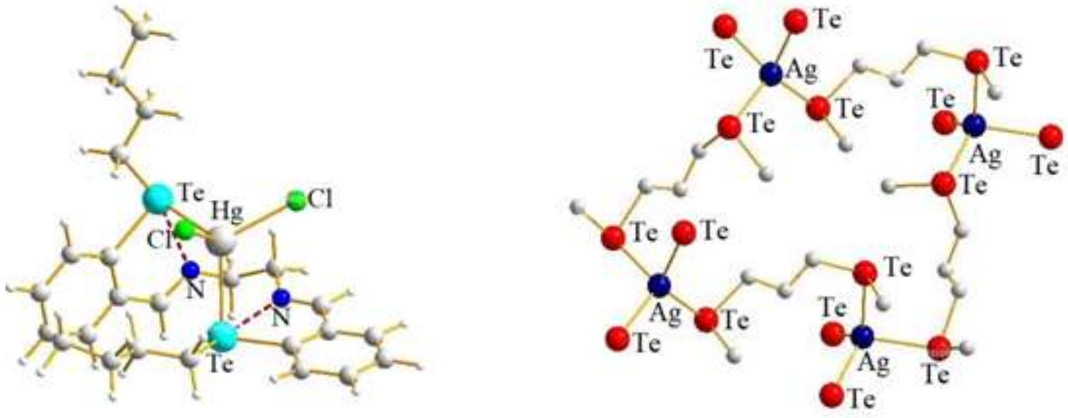
When mercuric chloride interacts with L^4, a macrocycle chelate ring with a Te-ligand emerged[3]. This process is depicted in Scheme 3 represents the initial instance of a crystallographically characterized macrocyclic chelation containing Te-ligand. The coordinating architecture of Hg^{II}, which has bonds to two Cl^- along with two Te donors, appears tetrahedral. Te^{II} functions as both a Lewis acid as well as a Lewis base at the same time because of unique presence of Hg-Te and Te┈┈N connections. Te^{II} exclusively connects to Hg^{II} in above arrangement, ignoring the possibility of Te-N binding to produce a 6-member chelate ring. It demonstrates Te-ligands' high predilection for 'soft' acidic centers. Owing to the N-lone pair's involvement in the development of the intramolecular Te┈┈N connection, the ligand's density has dropped. Every Ag^I ion within the polymeric Ag^I compound of L^5 is linked to four Te donors of the four bridging L^5 in the form of distorted tetrahedral fashion. The entire structure is made up of 24-member metallomacrocycles {$[Ag_4(L^5)_4]$ units}[4] [Figure 2].The structure has non-interacting $[BF_4]_n$ anions amid cationic $[Ag(L^5)_n]^{n+}$ layers. The repeating component is $[Ag_4(L^5)_4]$ ring. In the development of the polymeric composition $[Ag(L^5)]_n[BF_4]_n$, coordination of two Te donors of the ditelluroether, L^5 to Ag^I, are involved. Synthesis method is shown in Scheme 4. L^6 was formed along with its compounds $[MCl_2(L^6)]_2$ (M = Pd or Pt). According to studies of molecular weight along with conductance, the crystal arrangement of $[PtCl_2(L^6)]_2$ reveals a bimetallic combination of Pt^{II} with a 20-member metallomacrocycle ring that is stable in solution[5,6] [Figure 3].The pair of *trans*- Cl^- donors, the Te atom of one bridging ligand, the N atom from another bridging ligand and the square planar nature of the immediate surroundings around Pd in L^6 make up the structure of the complex. As a consequence, a metallomacrocycle ring with 20-members is formed [Figure 3]. The synthetic routes are shown in Scheme 5. Similar types of reactions are observed for L^7. Its synthesis and metal complex formations are displayed in Scheme 6.



Scheme 3



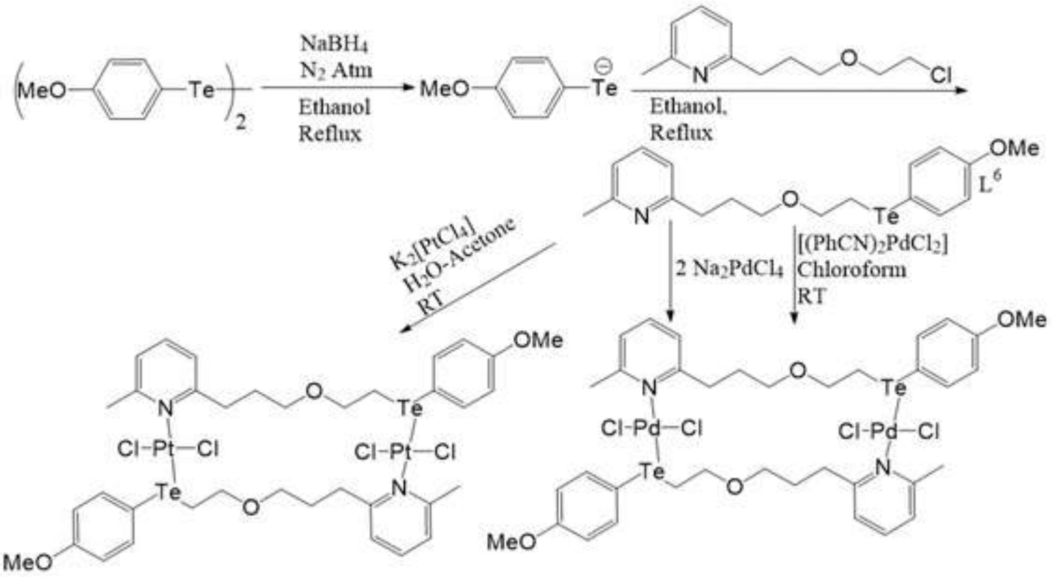
Scheme 4



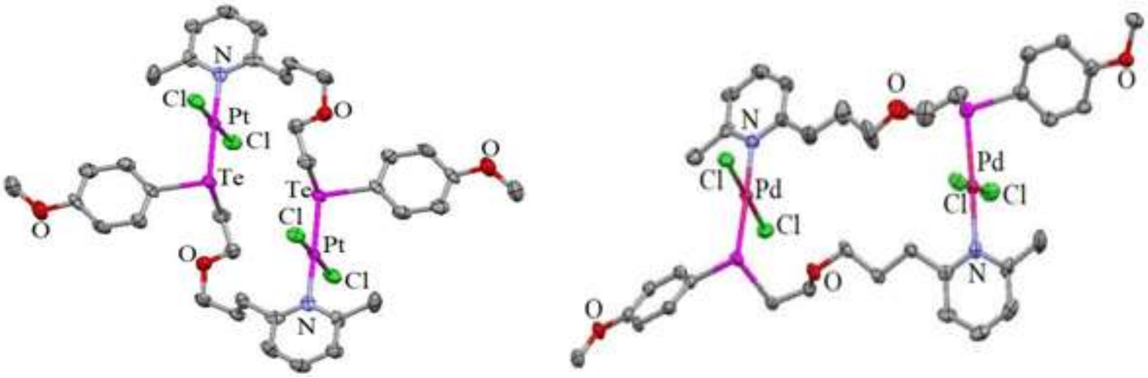
$[Hg(L^4)Cl2]$

Repeating unit of $[Ag_4(L^5)_4]_n$

Figure 2

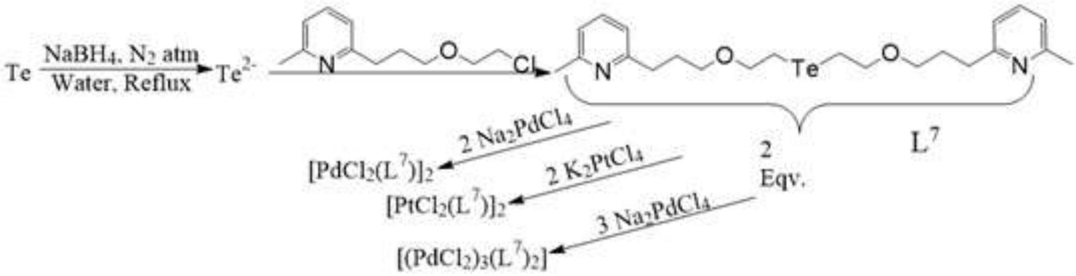


Scheme 5



$[PtCl_2(L^6)]_2$ $[PdCl_2(L^6)]_2$

Figure 3

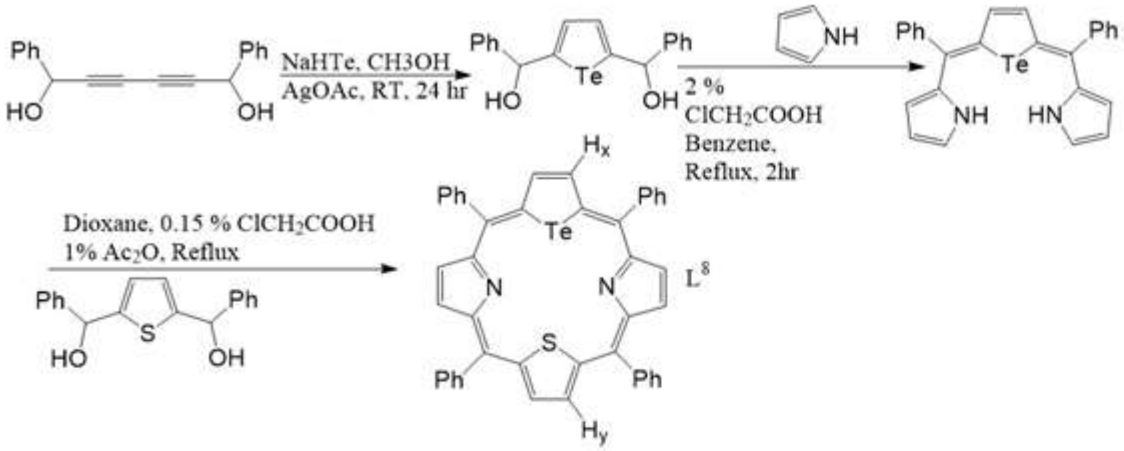


Scheme 6

IV. TELLURAPORPHYRINS

One Te atom is substituted instead of the NH component in the 21-position and is positioned opposing the NH or S atom in the 23-position within several core-modified porphyrins. 21-heteroatom-23-heteroatom interaction is enforced by the increased van der Waals radius of the heteroatoms inside the core-altered porphyrins.L^8 is the very first published core-modified Te-porphyrin[7] [Scheme 7]. From the crystal framework, it emerged that the Te┈┈S spacing (2.65 Å) was unusually low.

In hetero-substituted tetraphenylporphyrins, in which two NH groups in the central region have been substituted by S, Se, and Te, structural investigation reveals unusually close spacing among heteroatoms X and Y (X, Y = S, Se, Te), suggesting the existence of chemical associations among the heteroatoms [Figure 4]. High resolution NMR investigation supports these findings[8].



Scheme 7

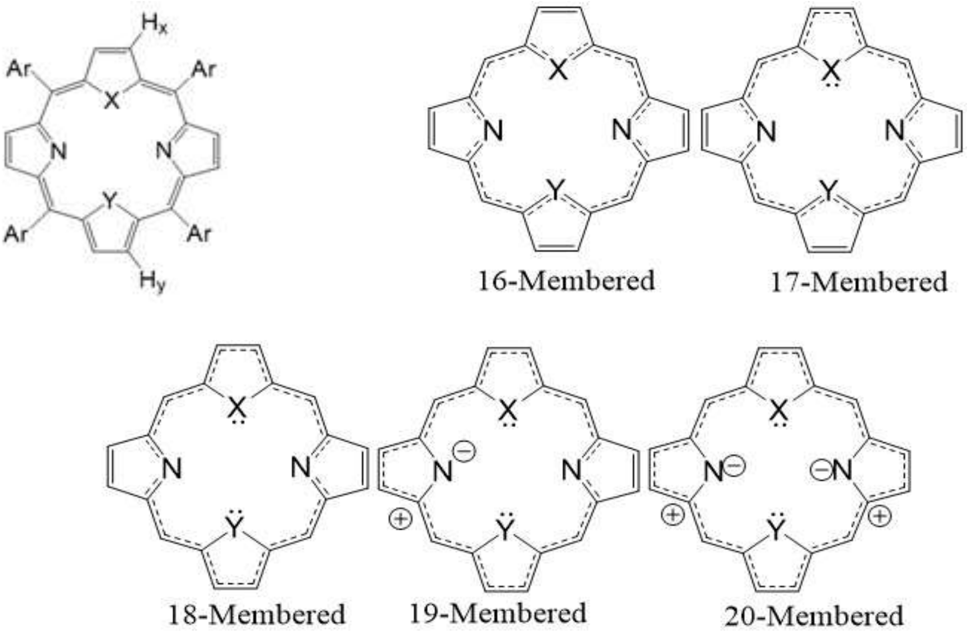
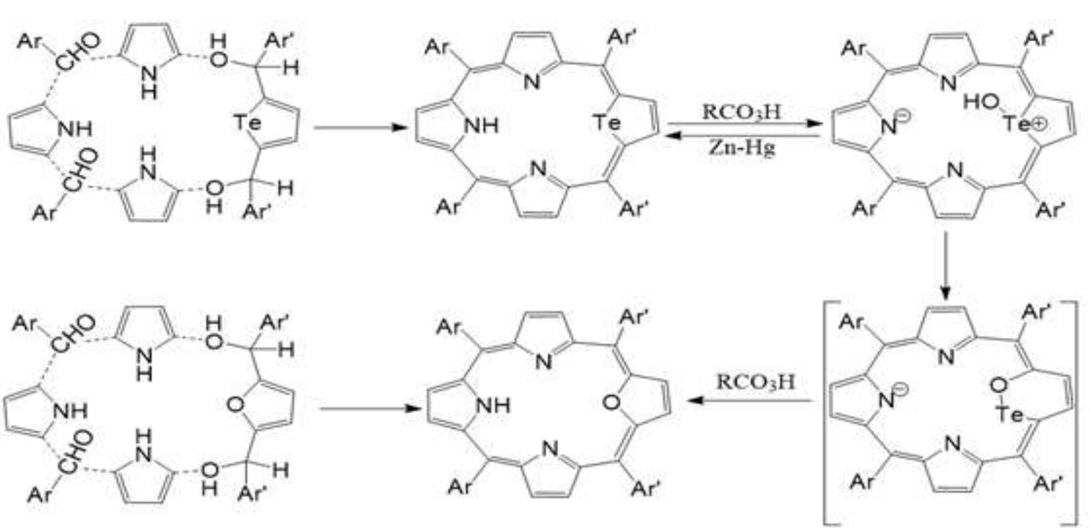
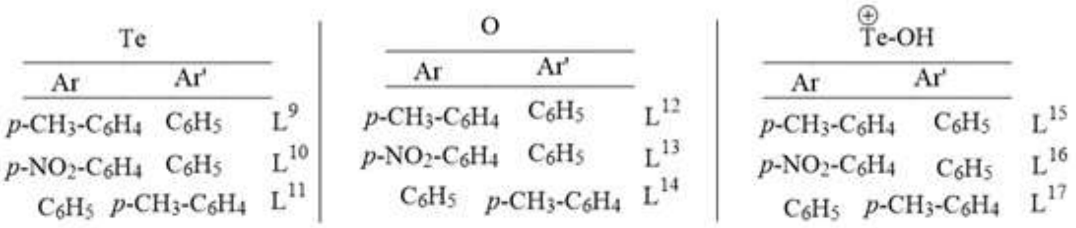


Figure 4

The inner as well as outer aromatic pathways of the porphyrin are altered by this interaction that rises in the sequence of S, Se, and Te and it also affects the chemical shifts of the H atoms; H_x and H_y along the molecule's edge[8]. The Kekulé structures of porphyrin provide an explanation for this. The potential Kekulé structures involving hetero-substituted porphyrins are depicted in Figure 4. The inner, outer, as well as extended outer aromatic pathways are represented by the 16-, 18-, and 20-member frameworks, respectively. As X······Y interaction grows, less electron density can be found on X and Y to support the interior aromatic route, increasing the statistical significance of the exterior (18-member) aromatic path. Due to their proximity to the exterior aromatic route, H_x and H_y exhibit downfield shifts in their NMR spectra in comparison with symmetrically substituted porphyrins. Such downfield shifts aren't caused due to heteroatoms' altering electronegativity, as was the case for free heterocycles. Here, H_x and H_y shifts upfield when the X······Y interaction inside the core is broken, either by protonation or complex formation. Such upfield shifts are caused by heteroatoms' complete electron densities contributing to the interior aromaticity, which lowers the likelihood of exterior aromaticity compared to its interior aromaticity. In L^8, the Te·····S interaction causes charge transfer from Te to S. Thiophene-H (H_y) of L^8 appears to move upfield in comparison to H_y of corresponding thia counterpart, since there is greater interior aromaticity via S in L^8 relative to the symmetrical thia counterpart. Similar to this, the inner aromatic route on Te has reduced electron density accessible, which causes H_x to shift downfield.

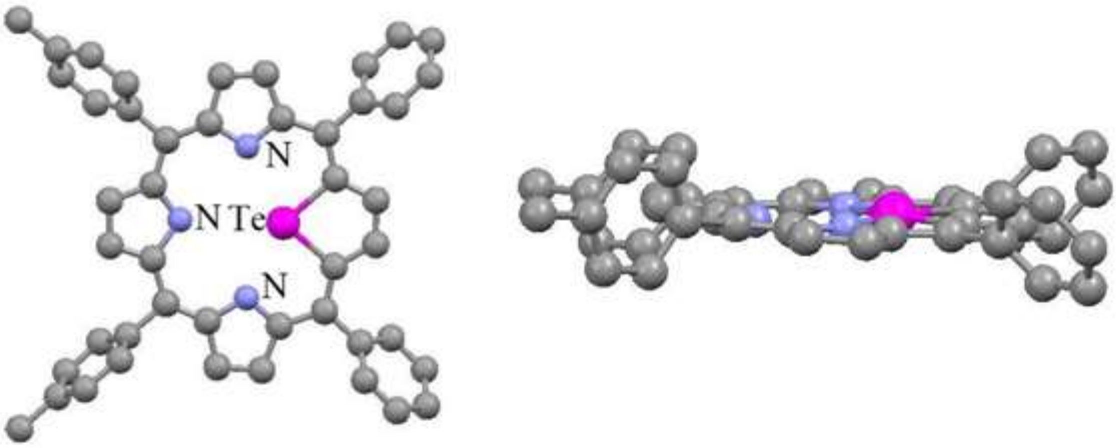
In accordance with Scheme 8, the 21-telluraporphyrin L^9were produced made. Because of the Te donor's higher diameter compared to a typical porphyrin, the molecular framework of L^9 exhibits a longer non-bonded N1·········N3 gap, distorting the framework. The porphyrinmacrocycle featuring an enormous core heteroatom is virtually planar in spite of its modest Te-N(2) gap [Figure 5][9].It demonstrates that, in contrast to the selenaporphyrin analogue, the tellurophene ring is involved in aromatic delocalization. The 21-telluraporphyrins [L^{9-11}] are generally air sensitive, compared to their thia and selena equivalents, and are capable of being changed into the 21-oxaporphyrins [L^{12-14}] by making use of m-chloroperoxybenzoic acid. The generation of a tellurium hydroxyl molecular structure [L^{15-17}] is how this process moves forward. The pyrrole ring is deprotonated by the O at the Te atom, yielding the molecules L^{15-17} containing -OH group at the Te center. It is unique regarding the chemical properties of tellurophene for the Te atom in L^{9-11} to easily get oxidized and then getting transformed into furan moieties [L^{12-14}] after exposure to a peroxy acid. The behaviors of the macrocycles L^{9-11} showed how significantly the porphyrin surroundings might change the tellurophene portion's fundamental activity. Telluroxide O gets protonated via the pyrrole NH *trans-* to the tellurophene ring, according to the crystal arrangement of L^{16}, which results in zwitterions containing a -OH group linked to the Te donor.The Te-O linkage passing across the porphyrin plane is L^{16}'s most intriguing architectural aspect. A weak H-bond is established between the Te-OH unit and the deprotonated N atom of the *trans-* pyrrole ring, which is tilted away from the plane in the direction of the -OH group.



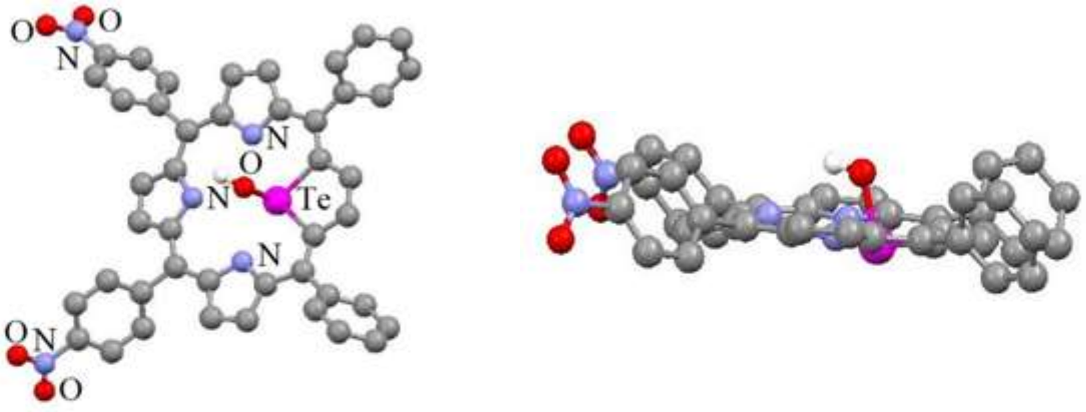


Te			O			$\overset{\oplus}{Te}$-OH		
Ar	Ar'		Ar	Ar'		Ar	Ar'	
p-CH_3-C_6H_4	C_6H_5	L^9	p-CH_3-C_6H_4	C_6H_5	L^{12}	p-CH_3-C_6H_4	C_6H_5	L^{15}
p-NO_2-C_6H_4	C_6H_5	L^{10}	p-NO_2-C_6H_4	C_6H_5	L^{13}	p-NO_2-C_6H_4	C_6H_5	L^{16}
C_6H_5	p-CH_3-C_6H_4	L^{11}	C_6H_5	p-CH_3-C_6H_4	L^{14}	C_6H_5	p-CH_3-C_6H_4	L^{17}

Scheme 8



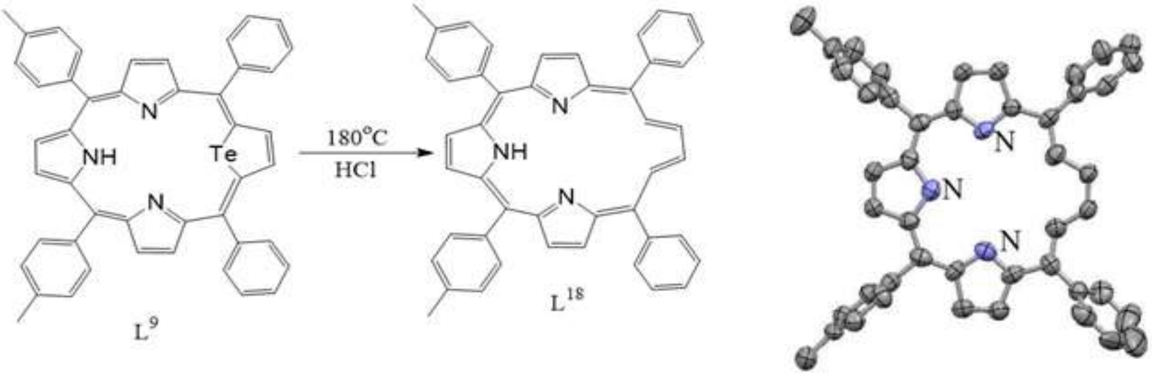
L^9 (Top View) Perpendicular L^9 (Side View)



L^{16} (Top View) L^{16} (Side View)

Figure 5

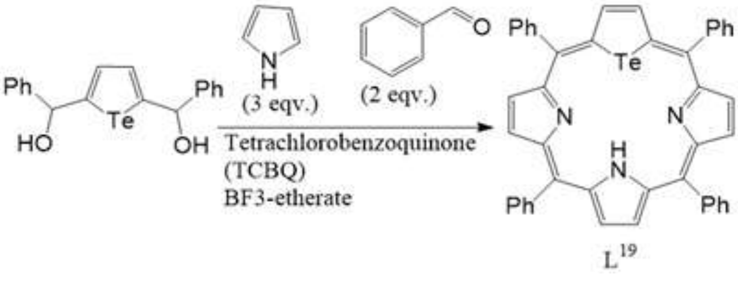
L^9 is anexcellentcandidate to synthesize a novel molecular structure, aza-deficient porphyrin L^{18}, by removing the Te donor from L^9 due to the unstable character of the C-Te-C segment[10] [Scheme 9].



Scheme 9

The catalyst enabling the activation of Hydrogen peroxide (H_2O_2) can be an organotelluride[11]. Mechanistic investigations have demonstrated that the first oxidation of organotelluride using H_2O_2 results in the formation of the Te^{IV} component; diorganodihydroxytellurane [$R_2Te(OH)_2$]. The organotelluride is subsequently generated through exchange of ligand, and followed by reductive elimination. Te containing 21- and 21,23-core-modified porphyrinsstabilises the Te^{IV} intermediates through obtaining lone pair of electrons from the heteroatom at location 23.

21-telluraporphyrin (L^{19}) is produced by the reaction between PhCHO, pyrrol, and 2,5-bis (phenylhydroxymethyl) tellurophene [Scheme 10]. The very same interaction, nevertheless, produces the oxidized Te-porphyrin (L^{20}) [Figure 6], byproduct of the chemical oxidation of L^{19} with air or H_2O_2, in the presence of light[12].Investigations using spectroscopy as well as cyclic voltammetry confirmed the straightforward aerial oxidation of L^{19}. Experiments using cyclic voltammetry reveal that L^{19} and L^8 undergo electrochemical oxidation at a greater negative potential compared to their lighter chalcogen counterparts. Such Facile oxidation happens due to bigger dimension of Te donor leading to deviation from planarity for L^{19} and L^8 resulting from interactions in solution of the type 21-Te-23-S/N. Using H_2O_2, the oxidation of L^{19} and L^8 progresses via second order rate constant. Each of these findings point to the significance of 21-telluraporphyrins as potential H_2O_2-activation catalysts. The 23-S/N helps with oxidation and functions as a backward donor to restrict access from one end, allowing oxidizable components to solely engage the Te donor site from the other side.



Scheme 10

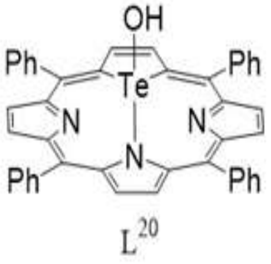
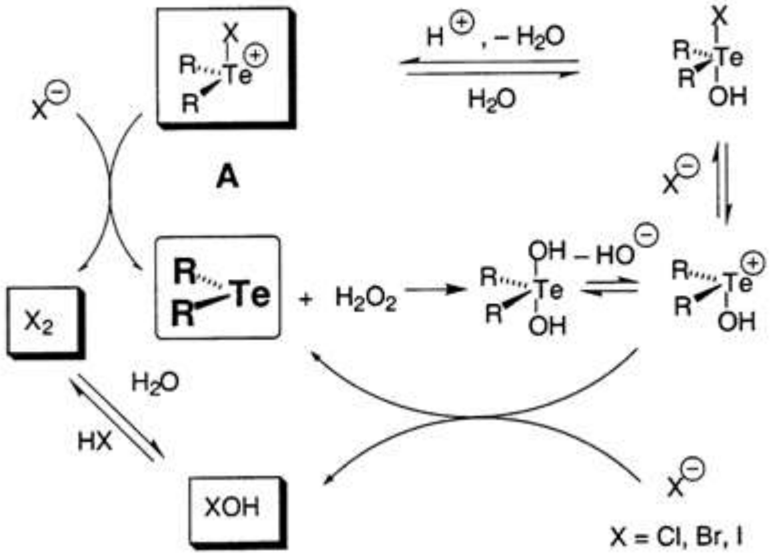


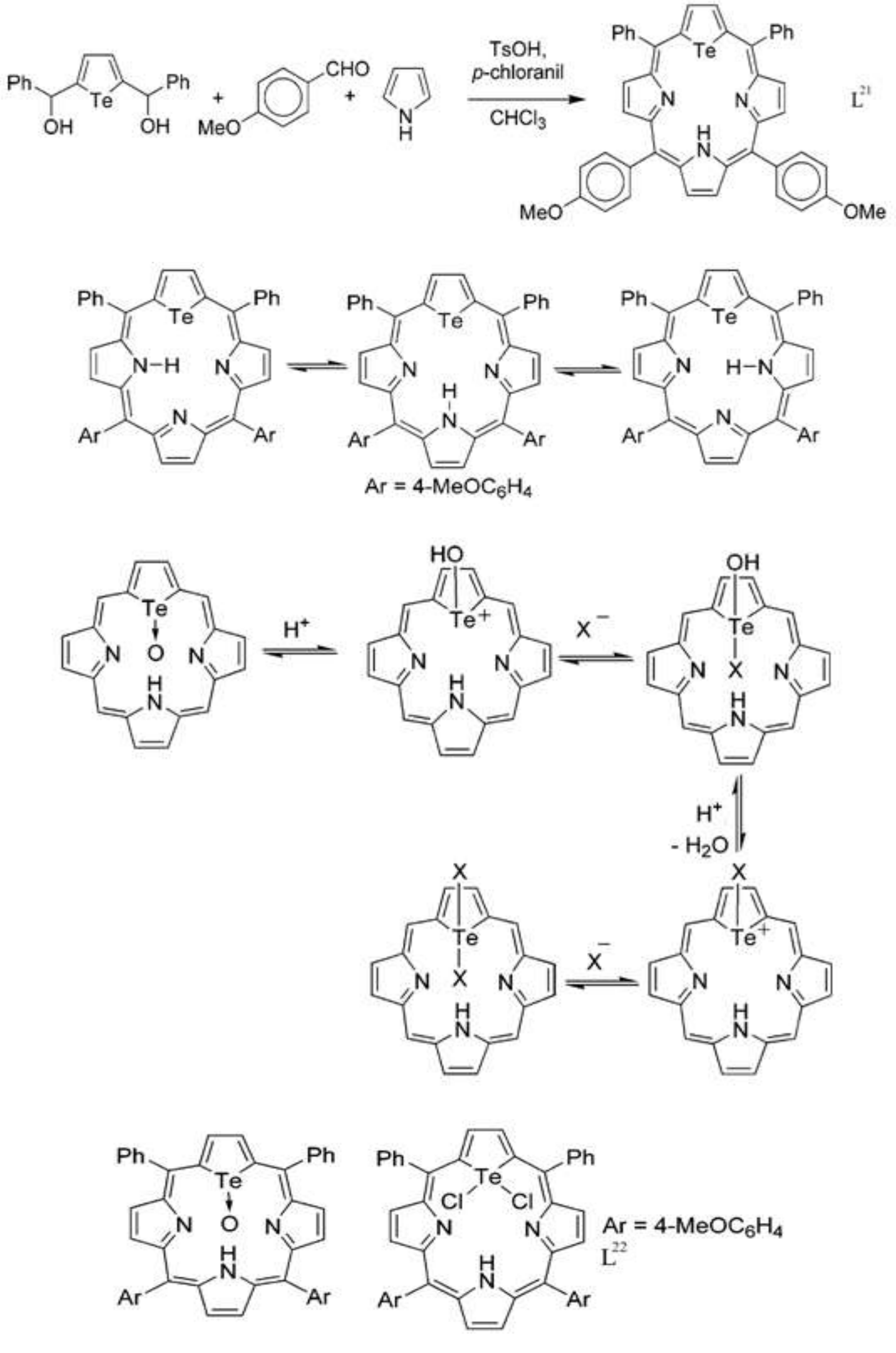
Figure 6

Additionally, the substances L^8 and L^{19} serve as catalysts during bromination processes involving H_2O_2 and NaBr reagents. Two situations, as shown in Scheme 11, are possible according to mechanistic investigations. L^8 is a significantly less effective catalyst compared to L^{19}. Unexpectedly using H_2O_2 and NaBr, for 21-S/Se-porphyrins or 21,23-S_2/Se_2-porphyrins, bromination of 4-pentenoic acid does not occur catalytically[13].

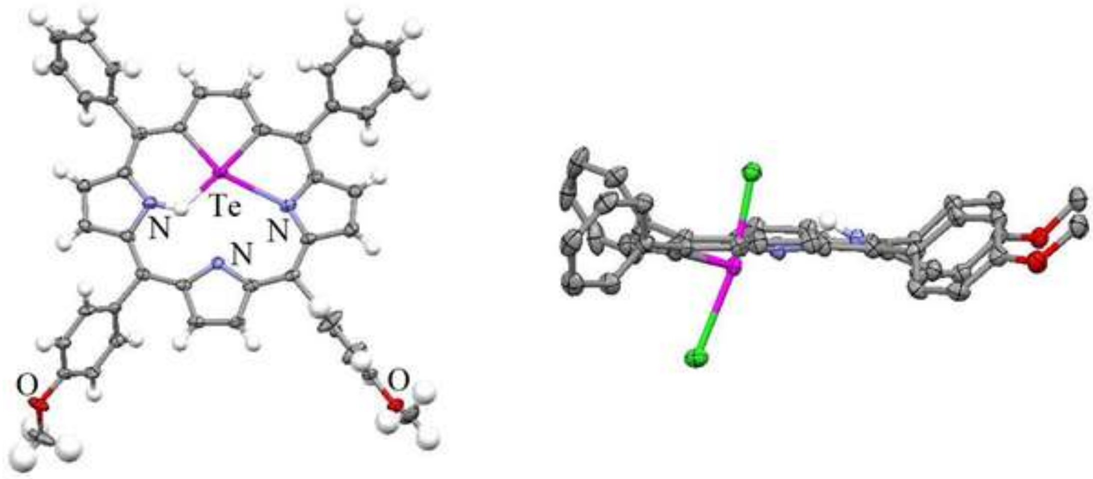
Additionally, researchers have produced one unique Te^{IV} derivative, L^{22}, and a Te-porphyrin of type L^{21} [Scheme 12]. There are three tautomeric versions of L^{21} because "H" atom of the -NH- is delocalized over all three pyrrole rings[14] [Scheme 12].When compared to other 21-Te-porphyrins, L^{21}'s structural framework [Figure 7] represents a tautomer where the pyrrole N-H *cis*- to the tellurophene. The porphyrin's center appears planar. L^{22} is produced by first oxidizing L^{21} to its equivalent telluroxide and then exchanging ligands using Cl^- as shown in Scheme 12. The Te-Cl linkages are located in *trans*-axial orientations, and the framework [Figure 7] exhibits Te in a deformed TBP configuration that is characteristic of $R_2Te^{IV}Cl_2$.Due to the higher stereochemical impact of the lone pair of electrons, which is evident by studying the <Cl-Te-Cl and <C-Te-C bond angles, the molecular structure is deformed from its perfect TBP shape. The VSEPR model's expectation and the real-world degree of bending in every other Te^{IV}macrocycles are both in agreement with each other. Since Te along with N; in *trans*- pyrrole, are both out of plane, a non-planarporphyrin center exists that is comparable to L^{16} but different from the planar center of L^{21} and L^9. The non-bonded Te1┈┈┈N2 separation in L^{22} is greater than the equivalent distance in L^{21} because the Te1 and N2 have gone out of the plane in L^{22}. Due to L^{22}'s tellurophene ring's deviation from planarity, the Te donor atom has no role in porphyrin's aromaticity here.



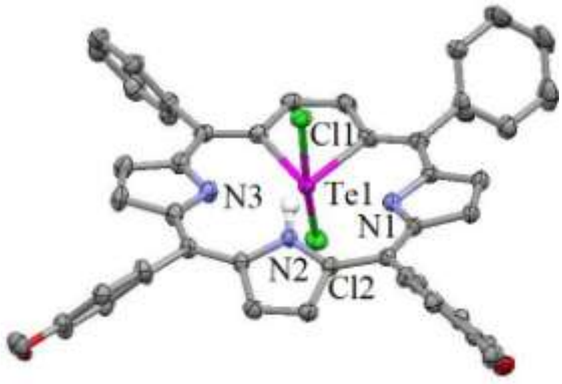
Scheme 11


TsOH,
p-chloranil
CHCl3
Ph
Te
OH
CHO
MeO
OMe
N
H
L21
Ar = 4-MeOC6H4
H+
X−
H+
- H2O
HO
OH
Te+
X
Cl
Ar
L22

Scheme 12



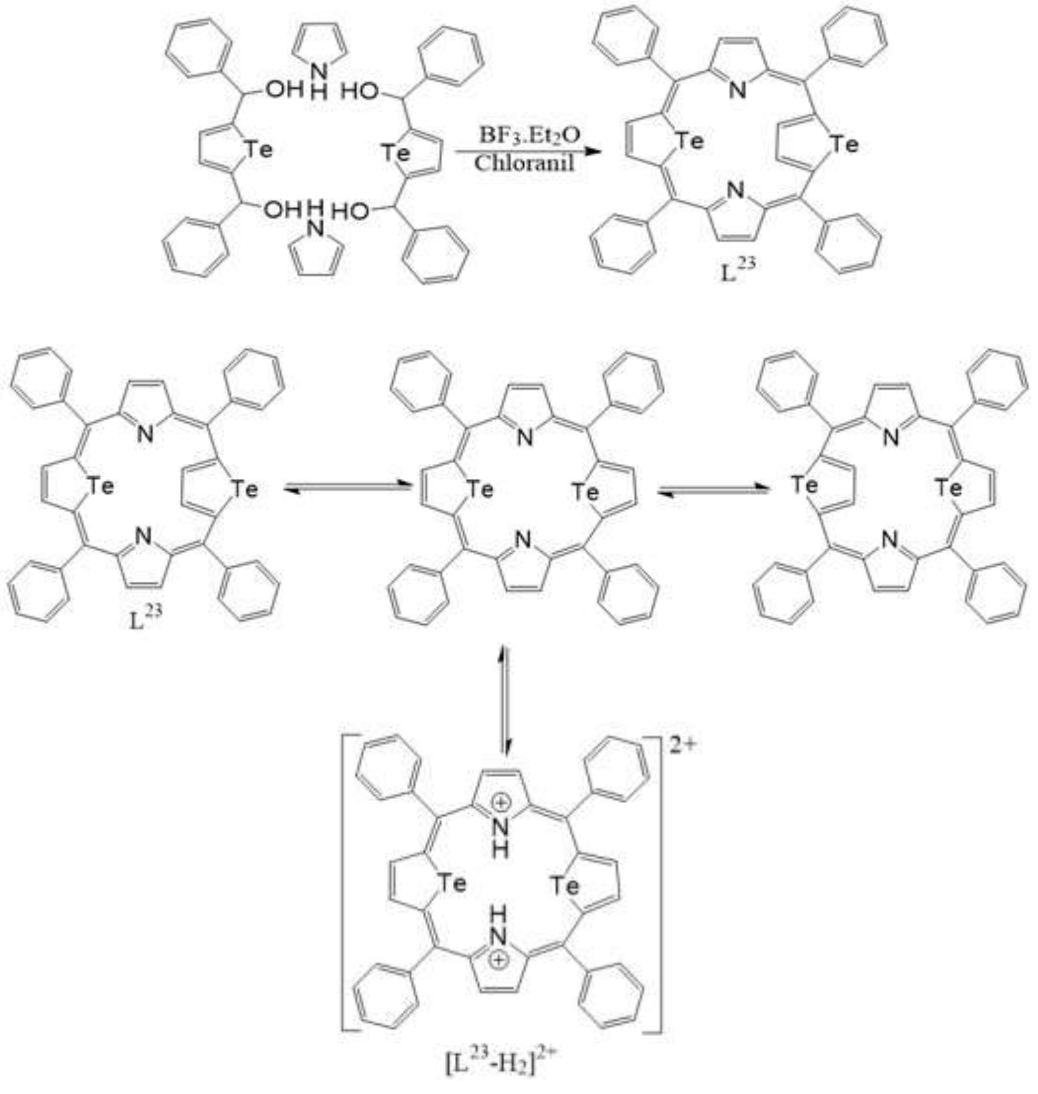
L^{21} L^{22} (Side View)



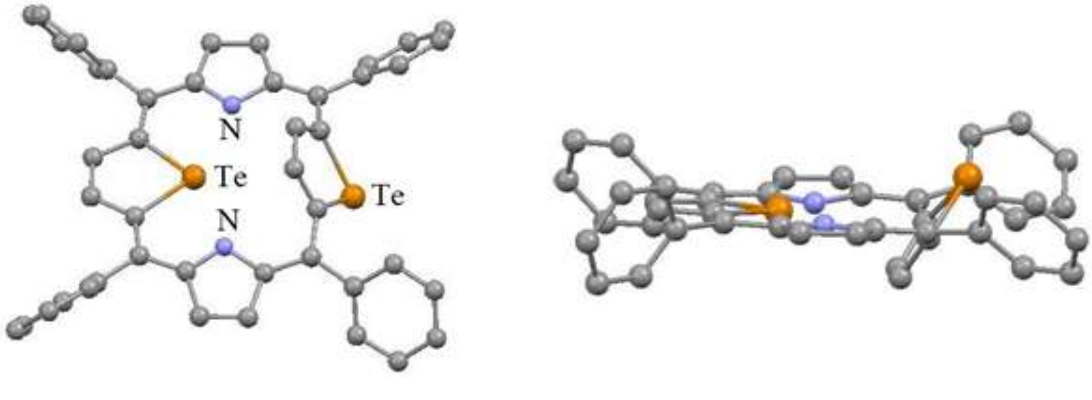
L^{22} (TopView)

Figure 7

In contrast to the O-/S-/Se- diheteroporphyrin, where both heteroatoms are situated towards the center within the macrocycle; for L^{23} one of the tellurophene moiety is coplanar with two nearby pyrrole rings whereas the other tellurophene is reversed and the Te donor atom is pointing out of the macrocycle [Figure 8][15]. The synthesis is shown in Scheme 13. The Te donor's massive diameter and the tellurophene ring's unique morphology as well as electronic structure both contribute to ditelluroporphyrin's distinctive properties. Despite not being aligned with the remainder of the macrocycle in L^{23}, the flipped ring is nevertheless significantly aromatic. 21,23-ditelluraporphyrin uses the same favoured 18-π-electron conjugation mechanism as those seen in mono-heteroporphyrins. According to Scheme 13, both tellurophene rings rapidly invert in solution. When ditellurophenes are titrated using trifluoroacetic acid (TFA), their configuration undergoes a major transformation that involves a reorganization towards the usual configuration, where both Te donors are pointed concurrently towards the core of the macrocycle. Due to the steric crowding, a substantial puckering of the macrocycle is anticipated, along with significant shifts of both tellurophene rings from the median plane.



Scheme 13



L^{23} (Top View)

L^{23} (Side View)

Figure 8

V. CONCLUSION

In conclusion, some important homoleptic macrocyclic polytelluroethers and tellurometallomacrocycles or telluro macrocyclic chelates were discussed thoroughly. Later focus was shifted towards telluraporphyrins. The 21- and 21,23-core-modified porphyrins having Te, are an intriguing category of compounds. The stability of the compound depends on its bonding connections among the heteroatoms inside the porphyrin nucleus[7]. For instance, by destroying the inner core communication/ interactions, such as protonation of the N atoms as well as complexation reduce the stability of the species[8]. In essence, the Te donor's massive size occupies its center and hinders endocyclic coupling with metals. When H_2O_2 and NaBr are added for bromination processes, 21-telluraporphyrins serve as catalysts. Inside core-modified Te-porphyrin surroundings, a peculiar change in the reactivity of tellurophene is seen.

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