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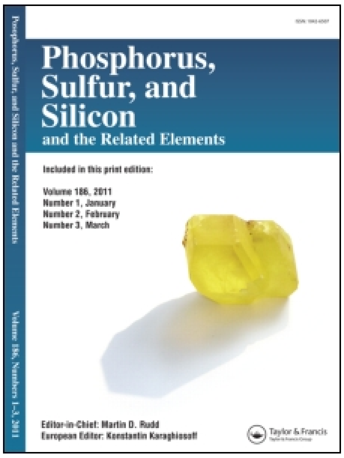

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Control of Selenocyclisations

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Control of Selenocyclisations

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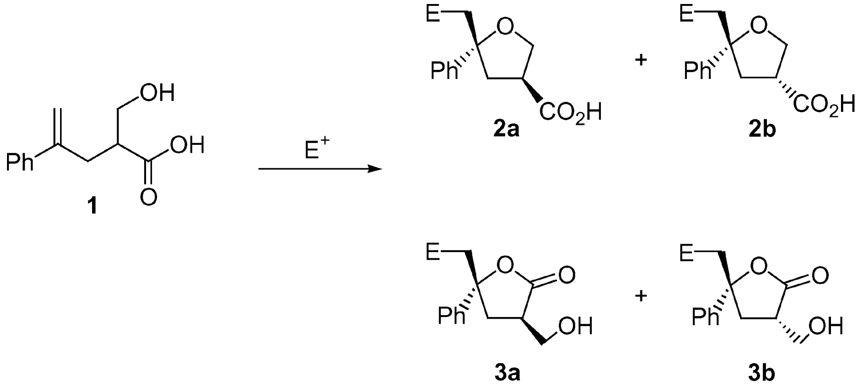
Chiral selenium electrophiles can be employed in cyclization reactions for the stereoselective synthesis of different heterocyclic compounds which are of great interest.[1] The effect of counterions in selenenylations and the interactions of selenium electrophiles with nearby heteroatoms have been reported earlier, but these observations do not yet give a conclusive picture.

We recently observed interesting effects of external nucleophiles on the course of selenenylation reactions. To investigate in which way different nucleophiles solvents and counterions affect selenocyclizations, we synthesised alkene **1**, which contains two different functional groups, an alcohol group and a carboxylic acid function.



SCHEME 1

Electrophilic 5-*exo*-cyclization of **1** can lead to either tetrahydrofurans **2** or to lactones **3**, depending on the attacking nucleophile (Scheme 1). The relative stereochemistry could not be resolved by NOE due to overlapping signals of **2** and **3**, which are both obtained as mixture of *cis* (**2a**, **3a**) and *trans* isomers (**2b**, **3b**). An X-ray crystallographic analysis of **3a** (E = I) finally allowed an unambiguous assignment. We will discuss the behavior of solvents, interactions of nucleophiles, and counterions with selenium electrophiles, which strongly affect the course of cyclizations.

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Studies on Selenocysteine Containing Active Site Peptides of Thioredoxin Reductase

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Selenocysteine is a naturally-occurring amino acid that constitutes the catalytic residue of some redox enzymes such as mammalian thioredoxin reductase and glutathione peroxidase. To study the effect of replacement of cysteine with selenocysteine on the local conformation and redox potential, we choose to investigate a set of model peptides containing S-S, S-Se, and Se-Se bridges.

N-9-Fluorenylmethoxycarbonyl-Se-4-methoxybenzylselenocysteine pentafluorophenylester [Fmoc-Sec(MBzl)-Opfp] was synthesized from selenocystine and successfully applied to Fmoc/t-Bu based solid-phase peptide synthesis. Two sets of C-terminal amide fragments of the enzyme thioredoxin Reductase from *Ratus ratus* and *Caenorhabditis elegans* were synthesized.

1. H_2N-DILQSGC(Acm)C(Acm)G-$CONH_2$
2. H_2N-DILQSGC(MBzl)Sec(MBzl)G-$CONH_2$
3. H_2N-LQGASGC(Acm)C(Acm)G-$CONH_2$
4. H_2N-LQGASGC(MBzl)Sec(MBzl)G-$CONH_2$

Three tetrapeptides corresponding to the active site variants of the enzyme thioredoxin were also synthesized. The Acetamidomethyl (Acm) protected cysteine peptides were oxidized by Thallium trifluoroacetate while para-methoxybenzyl (MBzl) protected selenocysteine peptides were oxidized by DMSO/TFA system to generate the S-S, S-Se, and the Se-Se bridged peptides.

The conformations of the peptides were probed by 2D-NMR and CD spectropolarimetry and the results are presented in this article.

Bis(*p*-Substituted Benzoylmethyl) Tellurides: Oxidative Additions and Ligational Behaviour

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Bis(*p*-substituted benzoylmethyl) tellurides, $(p\text{-}YC_6H_4COCH_2)_2Te$ ($Y = H$, Me), prepared by the reduction of the corresponding dibromides, $(p\text{-}YC_6H_4COCH_2)_2TeBr_2$, with $Na_2S_2O_5$ in an aqueous/organic phase, undergo oxidative addition reaction with ICl and $(SCN)_2$. Direct interaction of these telluroethers with d^8 metal centers Pt(II), Pd(II) resulted in the formation of complexes with 2:1 (ligand:metal) stoichiometry.

Simple alkyl/aryl tellurium halides readily undergo metathetical reactions with silver salts.[1] Analogous reaction of $(p\text{-}YC_6H_4COCH_2)_2 TeBr_2$, **1** ($Y = H$, a; Me, b) with AgX resulted in separation of tellurium metal. Alternative routes were therefore required to prepare the mixed halides and pseudohalides, $(p\text{-}YC_6H_4COCH_2)_2TeXY$. **1** are therefore reduces to $(p\text{-}YC_6H_4COCH_2)_2Te$, **2** which undergo oxidative addition reaction with ICl and $(SCN)_2$ to form the corresponding organotellurium halide/pseudohalide. Thus, reaction of **2** with $(SCN)_2$ at 0°C provided sparingly-soluble $(p\text{-}YC_6H_4COCH_2)_2Te(NCS)_2$ which appear to be N-bonded (IR spectra).[2]

Alkyltelluroethers are reported[3] to act as Lewis base towards metal halides and carbonyls. To explore the ligational behavior of **2**, these were reacted with a few d^8 and d^{10} metal systems such as Pd(II), Pt(II), and Hg(II). When a solution of **2** (0.82 mmol) in dichloromethane was stirred with $PtCl_2(PhCN)_2$ (0.4 mmol) in the same solvent, a clear solution resulted after ~2.5 h. Concentration of the reaction mixture and addition of pet. ether afforded dark brown adduct $PtCl_2(TeR_2)_2$ ($R = p\text{-}YC_6H_4COCH_2$) in over 80% yield. $PdCl_2(TeR_2)_2$ were prepared similarly. These adducts are sparingly soluble in CH_2Cl_2 and $CHCl_3$. As there is no negative shift in ν(CO) in adducts with respect to that of[4] **2**, it may be concluded that carbonyl oxygen atoms do not participate in the coordinative interaction with Pt(II) or Pd(II).

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Synthesis and Characterization of 1-Naphthylselenomethanes and Crystal Structure of 1-Naphthylseleno(phenyl)methane

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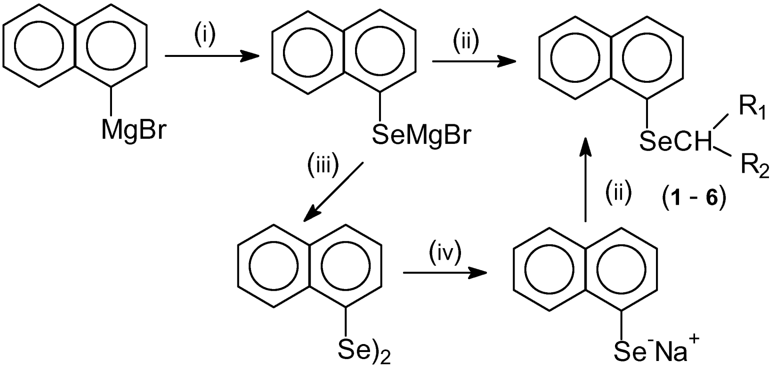
Organoselenium compounds, especially the mixed aryl alkyl selenides, have emerged as versatile synthons and find extensive application in organic synthesis, biochemistry, medicine, organic superconductors, and semi-conducting materials. A number of 1-naphthylselenomethanes have been synthesized by the *in situ* alkylation of 1-naphthylselenomagnesiumbromide, which in turn can be generated either by the oxidative addition of elemental selenium into 1-napthylmagnesium bromide in THF or by the direct alkylation of sodium 1-naphthylselenolate generated by the reductive cleavage of bis(1-naphthyl)diselenide using alkaline hydrazine hydrate in DMF at room



(Reaction methodology: Reagents and conditions (i)Se, THF (anhy.), reflux (ii) R_1R_2CHX 0–5°C (iii) H^+/H_2O [O] (iv) N_2H_4, H_2O, NaOH, DMF, r.t.

SCHEME 1

temperature. Both methodologies afford good yield of the titled compounds viz 1-$C_{10}H_7SeCH_3$ (**1**),1-$C_{10}H_7SeCH_2C_6H_5$ (**2**),1-$C_{10}H_7SeCH(C_6H_5)_2$ (**3**),1-$C_{10}H_7SeCH_2CH_3$ (**4**),1-$C_{10}H_7SeCH_2CH{=}CH_2$ (**5**),1-$C_{10}H_7SeCH_2CH_2NEt_2$ (**6**),(1-$C_{10}H_7Se)_2CH_2$ (**7**) and (1-$C_{10}H_7Se)_3CH$ (**8**). All the compounds prepared have been characterized by elemental analysis and various spectroscopic techniques viz., NMR (^{1}H, ^{13}C, ^{77}Se), U.V.-Vis, IR and mass spectrometry.

The procedural details and advantages of one method over the other have been discussed. The preparation and characterization of some bis(1-napthylseleno)alkanes has also been achieved. Crystal structure of (**2**) (Scheme 1) has been described.

Protection against Peroxynitrite-Mediated Nitration Reaction by Intramolecular Coordinated Diorganylselenides

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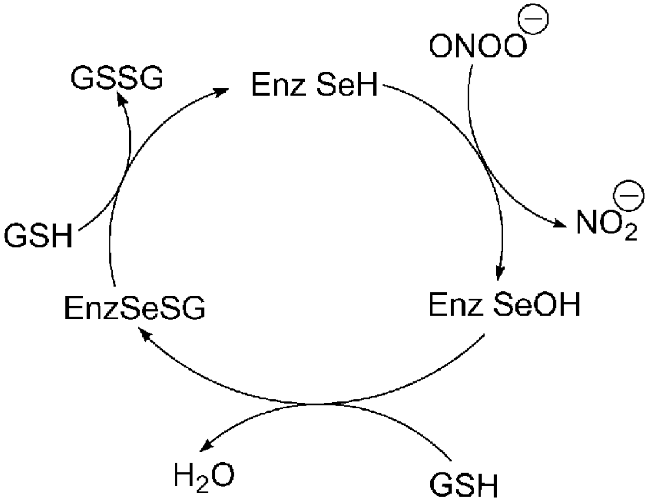
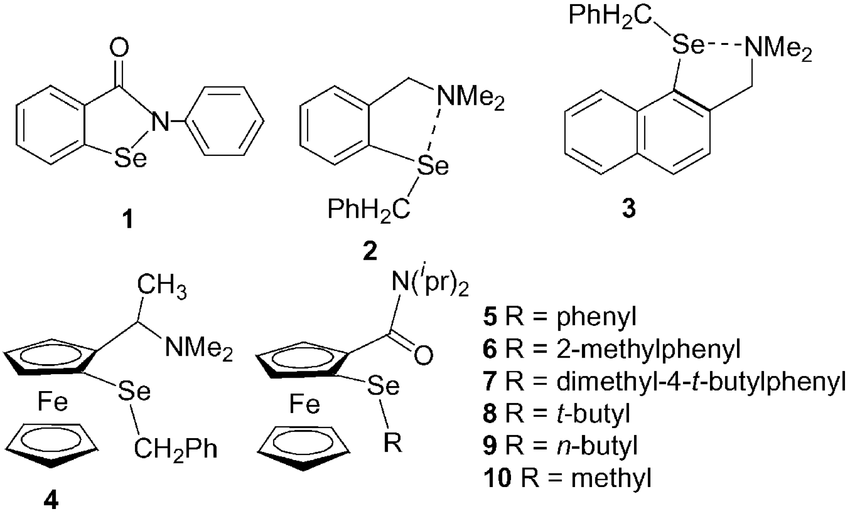
Peroxynitrite ($ONOO^-/ONOOH$) (PN) is a potent biological oxidizing agent.[1] The excessive production of PN can damage normal tissue and induces DNA damages as well as initiates lipid peroxidation in biomembrane or low density lipoprotein.[2] Its high reactivity of PN implicates its many disease states. Therefore it is important to search for the drugs that can defense against PN and detoxify it. The selenoproteins and synthetic Ebselen (**1**) compound have been proposed to act against PN effectively (Scheme 1).[3] Here we wish to describe the antioxidant property of few intramolecularly Se... X (X = O, N) coordinated diorganoselenides (Chart 1)[4] incluiding ferrocene (redox active group) in PN-mediated nitration reaction. This study revels that the abilities of selenides (**2–10**), which have basic amino groups in close proximity of selenium to protect against nitration reaction caused by PN are more efficient than the Ebselen and oxazoline, oxazine, and amide based selenides.

Therefore, basic nitrogen atom in model compounds in addition to the presence of electron donating group should positioned in such a



SCHEME 1



5 R = phenyl
6 R = 2-methylphenyl
7 R = dimethyl-4-*t*-butylphenyl
8 R = *t*-butyl
9 R = *n*-butyl
10 R = methyl

CHART 1

way that it should (i) increase the nucleophilicity of selenium atom, and (ii) increase the solubility of compound in aqueous solution.

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Influence of Organic Derivatives of Chalcogens on the Physical Properties of Water-in-Oil Microemulsions

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The effect of the addition of organic derivatives of chalcogens *viz.* diphenyl and dipyridyl selenides/tellurides on the properties of the AOT–Isooctane–Water system has been studied with the help of conductivity, FT-IR, and UV-visible spectroscopy. The influence of temperature and different concentrations of chalcogens on the physical properties has been analyzed. The concentration of the additive taken was 30 mM $\omega = 22.5$ and [AOT] = 0.415 M. The values of percolation temperature, T_c, estimated from conductivity results for all the systems vary in the order Py < Without Additive < Py_2Se_2 < Ph_2Se_2 < Ph_2Te_2. A comparison of pyridine and Py_2Se_2-based systems with the microemulsion without additive reveals that while pyridine favors percolation, the presence of Py_2Se_2 delays the percolation. Formulated systems have also been investigated using FT-IR and UV-visible spectroscopic techniques. The hydration of surfactant in reverse micelles and microemulsions can be observed through the shift in —OH stretching in FT-IR spectra. A comparative analysis has been done for Py_2Se_2, Ph_2Se_2, and Ph_2Te_2 to analyze the solubilization process of water. The UV-visible spectra has been recorded for the two microemulsion systems containing Ph_2Se_2 and Ph_2Te_2.

Removal of Selenium and Preparation of 7N Tellurium for Optoelectronic Device Applications

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Mercury Cadmium Telluride (MCT) is the most important compound semiconductor material for making Infra Red Detectors (IRDs) and are efficient in a wide wave length range of 1 to 20 μm.[1] Ultrapure (7N) tellurium (Te) is one of the major constitutes in CdTe and CdZnTe substrates preparation. Major applications of Te-based electronic substrates include night vision cameras and thermal imaging devices, which are predominantly used by armies during night-time operations. Using different physical processes, different IRDs can be fabricated, which can operate in a wide temperature range ($\sim$80–300°C). Inside the IRD, the charge carrier's mean termination time in a trap or recombination center (carrier life time) is strongly dependent on the impurity concentration, which will create deep levels in the energy gap.[2]

Tellurium metal can be purified from 4N pure to more than 6N (99.9999%) and above using in-house fabricated horizontal zone refiner[3] and is relatively easy metal to purify by zone refining due to most of its impurities having segregation coefficient $\ll$1, a high melting point (451°C) and low thermal conductivity. This Te was further purified in our laboratory using narrow zone widths by placing reflectors inside the cylindrical zone heaters under clean room conditions. The impurities analysis of purified tellurium was found to be matching with the specifications of 7N tellurium available, internationally. Selenium impurity content in tellurium matrix was generally removed by passing hydrogen gas on to the molten liquid of tellurium, as it can not be removed by zone refining due to nearly unity segregation coefficient. All metallic and nonmetallic impurities in ultrapure Te were analyzed using Glow Discharge Mass Spectrometry (GDMS) at the National Research Centre (NRC), Canada. However, the reported selenium content was analyzed using Inductively Coupled Plasma Analyzer Mass Spectrometry (ICPMS) which was locally available. The final content of selenium was reduced from 115 ppm to 20 ppb. The material thus developed can be used in the fabrication of IRDs. The process methodology and the analysis results of ultrapure tellurium is discussed in comparison with other published works from world pioneer laboratories.

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The Role of Coordination in the Structural Features of Organoselenolates

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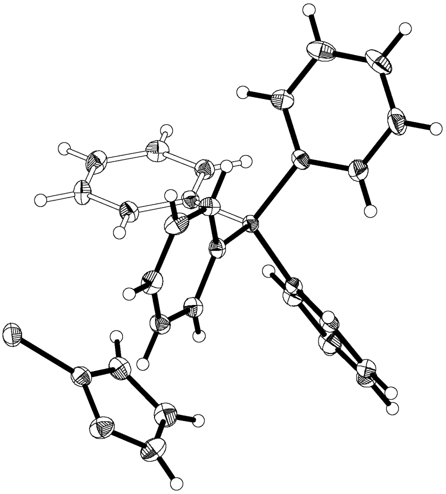
We recently have investigated the structural and chemical properties of transition metal complexes involving different organoselenolato- and -tellurolato ligands.[1,2] In this contribution we report the structural characterization of a series of uncoordinated organoselenolate ions of which the information is still rather sparse and generally involves their isolation and crystallization by using alkali metal cations that have been encapsulated by different crown ethers.[3,4] We have crystallized these anions using a weakly-polarizing tetraphenylphosphonium cation. The X-ray structures (Scheme 1) indicate the anions are well separated from the cations in the lattice and the packing is governed by the cations. The NMR spectroscopic properties, as well as



SCHEME 1

structural parameters of the uncoordinated organoselenolate anions, are discussed and compared to those of the bridging and terminal ligands in various transition metal complexes.

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Versatile Coordination Property of Chalcogenaaza Macrocycle: HSAB Principle or Chelate Effect?

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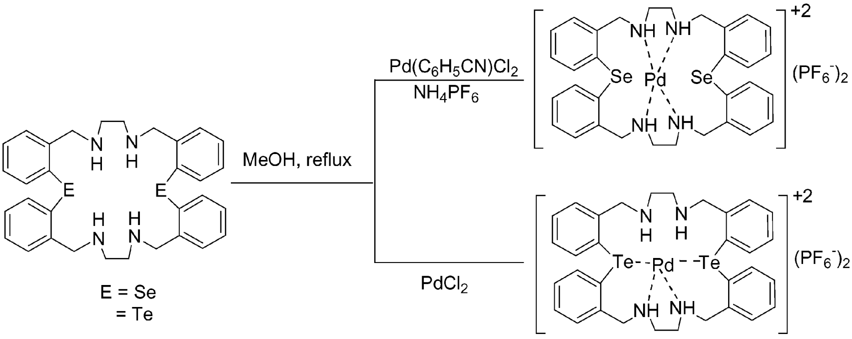
Macrocyclic ligands have been attracting much interest due to their exceptional complexation potential, which has facilitated the study of metals in unusual circumstances, such as uncommon coordination numbers, coordination geometries, and donor atoms or oxidation states.[1] In



SCHEME 1

the last few years we have been interested in Schiff-base chalcogenaaza-macrocyclic ligands and their coordination properties with late transition metals.[2–4] Herein we describe a few examples (Scheme 1) of versatile coordination property of selena/telluraaza macrocycles towards transition metal ions.[5–7]

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Glutathione Peroxidase-Like Antioxident Activity of Organotellurium Compounds: Novel Structures and Catalytic Mechenisms

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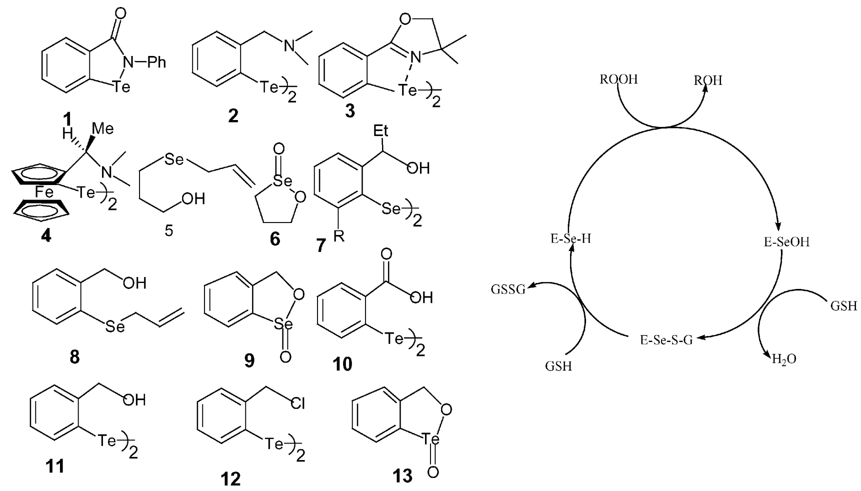
The chemical and biological importance of tellurium has attracted considereable attention as evidenced by several model studies on the antioxident and photochemotherapeutic properties of synthetic organotellurium compounds. The tellurium compounds are more attractive towards antioxident behavior because tellurium is more nucleophilic than the sulfur, and thus the molecules containing it can react faster with electrophilic compounds as free radicals. Herein, we report the preparation, characterization, and evaluation of their catalytic activity and related mechanistic study of a series of intramolecularly coordinated



SCHEME 1

diorganyl ditellurides (Scheme 1) and tellurininate ester compared with diselenides.