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Aspects of organochalcogen (S, Se, Te) compounds stabilized by intramolecular coordination

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Abstract. The application of intramolecular coordination in the isolation of novel diaryl diselenides and their derivatives, monomeric chalcogenolato complexes of group 12 metals, glutathione peroxidase mimics, hybrid bi-, tri- and multidentate ligands and selenium-containing azamacrocycles is described.

Keywords. Intramolecular coordination; metal chalcogenolates; glutathione peroxidase mimics; hybrid chalcogen ligands; selenium macrocycles.

1. Introduction

The chemistry of organochalcogen derivatives stabilized by intramolecular E···N (E = S, Se, Te) interactions has attracted considerable current interest [1]. Recent studies on intramolecularly stabilized organoselenium and tellurium compounds show that the Se···N and Te···N intramolecular interactions play an important role not only in the catalytic antioxidant activity of these compounds [2] but also in their application as reagents in synthetic organic chemistry [3]. The application of intramolecular coordination has been extended to the synthesis of novel organochalcogen ligands containing both 'hard' and 'soft' donor atoms [4]. The intramolecularly coordinating ligands have also been used for the isolation of monomeric metal chalcogenolates, in particular, the group 12 metal (Zn, Cd, Hg) chalcogenolates which are useful precursors for the metal organic chemical vapour deposition (MOCVD) of semiconducting materials [5]. These complexes are generally polymeric with bridging chalcogenolate ligands. More recently, considerable effort has been directed towards the design and 'template-free' synthesis of novel macrocycles containing selenium and tellurium and their coordination behaviour towards transition metal ions [6].

In this paper, we briefly discuss some recent results from our laboratory in the area of intramolecular coordination and its application in the synthesis and isolation of selenenyl halides, achiral and chiral selenium ligands, glutathione peroxidase-like antioxidants and novel selenium macrocycles.

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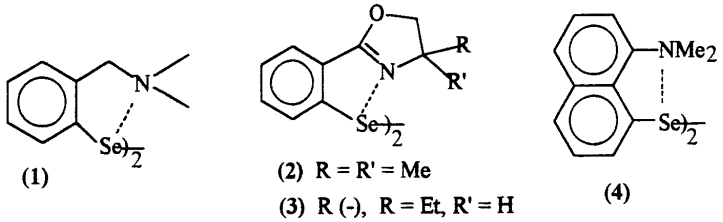
2. Results and discussion

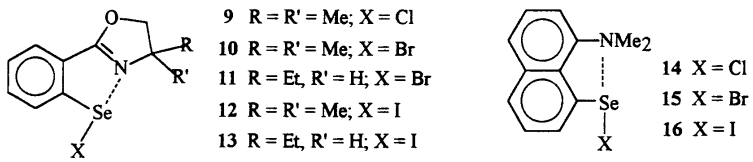
2.1 *Achiral and chiral diaryl diselenides and their halo derivatives stabilized by Se···N nonbonded interactions*

Organoselenium compounds, in particular those having Se···N intramolecular interactions are challenging targets for organic and organometallic chemists because of their role in chiral induction and catalytic conversions. Uemura *et al*[3f–h] have extensively used optically active ferrocenyl diselenides with in-built donor sp^3 nitrogen for very high chiral induction, whereas Tomoda *et al*[3i–k] have demonstrated in a series of papers that organoselenium derivatives with a coordinating amino group can be used not only for the catalytic conversion of olefins to allylic ethers but also for asymmetric inter- and intraoxyselenenylation reactions. Our group has reported the synthesis and structural characterisation of *bis*(2-dimethylaminomethyl)phenyl diselenide (**1**) and its use in the catalytic conversion of alkenes to allylic acetates[4d]. Recently, we have isolated and structurally characterized diselenides **2–4** in which the Se···N nonbonded interactions were found to be strong [Se···N distances (Å): **2**: 2·819(5) and 2·705(5); **3**: 2·798(5) and 2·780(5); **4**: 2·652(2) and 2·628(2)][7].

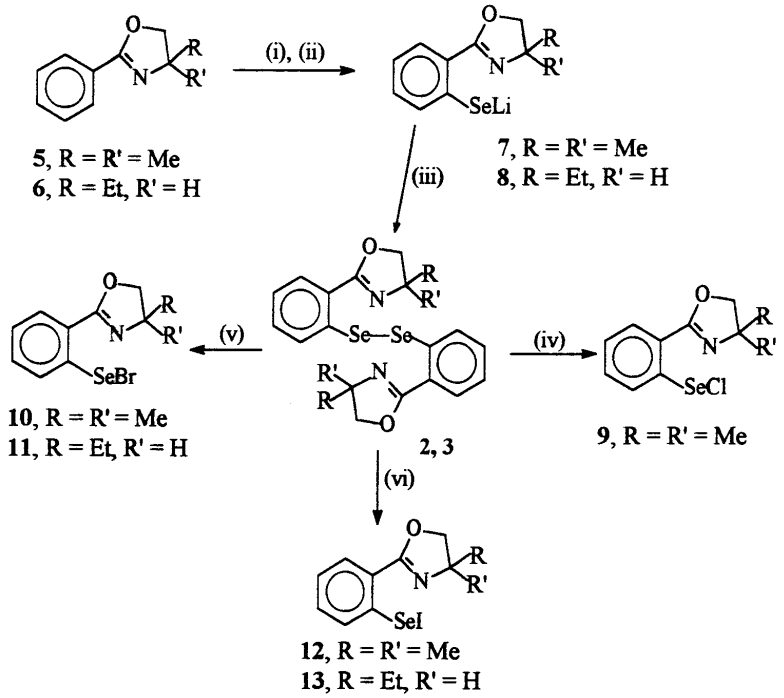


The synthesis of diselenides **2** and **3** was approached by the organolithium route. The lithium areneselenolates, $OxSe^{-}Li^{+}$ (**7**, **8**), were easily prepared by the direct metalation of 4,4′-dimethyl-2-phenyloxazoline (**5**) and R(–)-4-ethyl-2-phenyloxazoline (**6**) with *n*-BuLi in hexane followed by the addition of selenium powder in ether. Oxidation of the lithium selenolates then afforded the desired diselenides (scheme 1). Diselenide **4** was synthesised by a method similar to the one shown in scheme 1.

The synthetically useful selenenyl halides (**9–16**) were prepared by the reactions of diselenides with halogens (scheme 1)[8]. The stable chloro compound **9** was obtained as a crystalline solid in good yield by reacting the diselenide **2** with a stoichiometric amount of sulphuryl chloride. The bromo compounds **10** and **11** were synthesized by a similar method, with a stoichiometric amount of bromine. When the reactions of **2** and **3** were carried out with stoichiometric amounts of iodine, the novel monoiodides **12** and **13** were obtained. Compounds **14–16** were prepared by the reactions of diselenide **4** with Cl_2, Br_2 and I_2 respectively, in equimolar ratio.



In all these cases, the rigidity and planarity of the five-membered rings formed by the intramolecular Se···N interactions facilitate the Se···N interactions. These interactions lengthen the Se–X (X = Se, C, Cl, Br and I) bond *trans* to N–Se bond and increase the possibility of nucleophilic attack on the selenium atom. A correlation between the Se···N intramolecular distances and ^{77}Se NMR chemical shifts revealed that these interactions result in a downfield shift of the ^{77}Se NMR signals when there is a strong interaction. For example, the Se···N distances increase in the order **9** (2·052 Å) < **10** (2·063 Å) < **12** (2·133 Å), whereas the ^{77}Se chemical shifts decrease in the same order **9** (855·9 ppm) > **10** (849·5 ppm) > **12** (762·2 ppm). In addition to the synthetic applications, compounds **12**, **13** and **16** serve as the rare examples of stable selenenyl iodides. In contrast to other diselenides which form expected charge-transfer adducts with iodine [9], compounds **2–4** react with iodine to give stable binary compounds. In these cases, the formation of 10-Se-3 selane due to intramolecular stabilisation seems to be responsible for the formation of a covalent bond rather than charge-transfer adducts. Compounds **11** and **13** are the first examples of structurally characterized chiral selenenyl halides. These compounds may find applications in asymmetric synthesis as chiral organoselenenyl halides, in particular, those having Se···N or Se···O non-bonded interactions which are shown to act as electrophilic reagents in methoxy-selenenylation, aminoselenenylation and selenocyclisation reactions [3]. Chiral organoselenenyl halides having Se···O interactions have been recently used for the synthesis of natural products such as (+)-samine [10] and (+)-membrine [11].



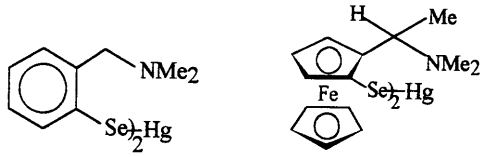
Scheme 1. Synthetic route to the [2-(4,4-dimethyl-2-oxazolinyl)phenyl]selenenyl halides **9–13**. Reagents and conditions: (i) *n*-BuLi, ether, 0°C, 4 h; (ii) Se powder, 0°C, 3 h; (iii) O_2, aq. $NaHCO_3$; (iv) SO_2Cl_2, CCl_4, 1 h; (iv) Br_2, CCl_4 0°C, 1 h; (iv) I_2, CCl_4, 0°C, 1 h.

2.2 *Monomeric chalcogenolato complexes of zinc, cadmium and mercury with nitrogen containing chelating ligands*

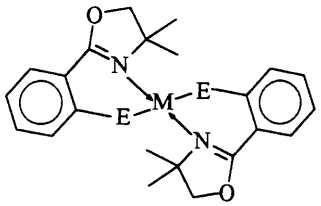
The chalcogenolate derivatives of Group 12 elements have recently attracted considerable attention because of their potential use as single source precursors to Group 12–16 semiconductors [12]. Unfortunately, the development of the molecular chemistry of these compounds has been slow as the precursors are often insoluble in common organic solvents due to the formation of non-crystalline polymers through bridging of the chalcogenolate ligands, and are therefore difficult to both purify and characterize. Among the several methods used to reduce the ligand association and enhance the volatility of the compounds, the use of bulky substituents has proved very effective [12e]. The main disadvantage in this method is that the chalcogenolate complexes of this type are known to involve in a reductive elimination process to give the dichalcogenide and elemental metal. Our approach to this problem involves the introduction of chalcogenolate ligands having covalently attached donor atoms for the isolation of the monomeric complexes. Using this approach, we have isolated some stable monomeric mercury selenolates (**17–19**) derived from N,N-dimethylbenzylamine and N,N-dimethylaminoethyl ferrocene [5d]. However, the monomeric zinc and cadmium selenolates could not be isolated using these flexible ligands. Therefore by using the more rigid (4,4-dimethyl-2-oxazolinyl)phenyl ligand [13], we have recently succeeded in isolating the chalcogenolato complexes of zinc, cadmium and mercury (**20–28**). Ortho-metallation and chalcogen insertion followed by reaction with anhydrous metal chlorides afforded the complexes in monomeric form.

Complexes **20** and **23**, which were obtained as yellow solids show some interesting features. The complexes afford two types of crystals; plates and needle-shaped crystals due to spontaneous resolution of racemates. The room-temperature ^{1}H NMR spectra of **20** and **23** contain a well resolved AB doublet-of-doublets for the methylene protons indicative of an inequivalence of these protons. The AB pattern implied that the strong coordination of the imine 'hard' nitrogen with 'hard' Zn(II) makes the protons diastereotopic, which in turn results in chirality of the complexes. Since the chirality is induced at the metal centre by helical distortion, this type of chirality is generally known as 'helical chirality' [14]. The cadmium thiolate, selenolate and tellurolate complexes showed chirality at low temperatures whereas the mercury thiolate and selenolate did not show any chirality even at –60°C. The solution behaviour of mercury tellurolate could not be determined due to its instability in solution. The chirality observed in these complexes either at room temperature or low temperatures therefore shows the general tendency of the intramolecularly coordinating 2-(4,4-dimethyloxazolinyl)phenyl ligand to form 'helical' metal complexes. In all these complexes, the formation of the six-membered chelate ring with metal seems to be an important factor in deciding the molecular nature of these compounds. As expected, the stability of the Group 12 metal complexes decreases in the order S > Se > Te. In addition to the 'helical' chirality, the low molecularity, excellent solubility in hydrocarbon solvents, low melting points and relatively high volatility of these complexes make them useful as single-source precursors to group 12–16 thin-film semiconductors. The thermal behaviour of these compounds has in fact, provided some insight into their utility for decomposition of thin films via chemical vapour deposition (CVD). While the TGA of zinc and cadmium thiolate and selenolate complexes showed the formation of expected metal sulfides (MS) and metal selenides (MSe) [M = Zn, Cd], the mercury complexes showed complete weight loss in this temperature range, probably due to their high volatility. A novel homoleptic Bi(III)

selenolate (**29**) incorporating the oxazoline ligand has also been synthesized and characterized by X-ray crystallography [15]. The most interesting feature in the structure of this compound is the observation of stereochemically active lone pair of electrons on the bismuth.



17 **18** [R,S;R,S] (+)
19 [S,R;S,R] (-)



20 E = S; M = Zn
21 E = S; M = Cd
22 E = S; M = Hg
23 E = Se; M = Zn
24 E = Se; M = Cd
25 E = Se; M = Hg
26 E = Te; M = Zn
27 E = Te; M = Cd
28 E = Te; M = Hg

The strong N → M coordination and the unusual stability of the compounds may arise from the fact that the lone pair of electrons present on the oxygen may be involved in a resonance contribution with the p-systems as shown in figure 1. The involvement of lone pair electrons present on the oxygen atom is confirmed from the X-ray crystal structures of complexes **20**, **21**, **23–25** in which both C–N and C–O bonds show similar double bond character.

2.3 *Glutathione peroxidase activity of diorgano diselenides*

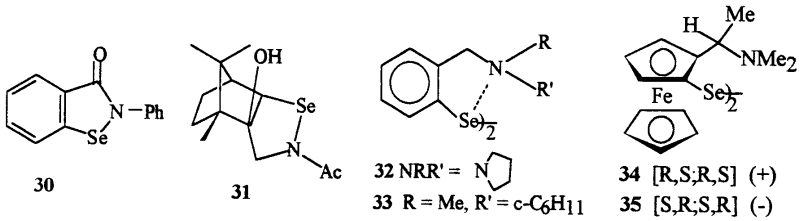
Glutathione peroxidase (GPx) is a well-known selenoenzyme which functions as an antioxidant [16]. This selenoprotein catalyzes the reduction of harmful peroxides by glutathione and protects cell membranes from oxidative damage. Recently much attention has been devoted to the synthesis of simple organoselenium compounds that mimic the action of GPx. Ebselen (**30**) [17], a heterocyclic compound containing Se–N bond, was the first compound of this kind. Other compounds such as selenenamide **31** [18], tellurides and ditellurides [19] were also shown to mimic the action of the natural enzyme. A synthetic selenoprotein, selenosubtilisn, has been reported to be 70,000 times more efficient than

A B

Figure 1. Postulated contribution of the oxygen atom to resonance stabilisation of the oxazoline ring in compounds **20–27**.

diphenyl diselenide in catalyzing the reduction of *tert*-butyl hydroperoxide in the presence of 3-carboxy-4-nitrophenyl mercaptan [20].

Recently, diaryl diselenides **1**, **32**, **33** with basic amino groups have attracted much attention as GPx mimics because the Se···N intramolecular nonbonded interactions (i) activate the Se–Se bond towards oxidative cleavage and (ii) stabilize the resulting selenenic acid intermediate against further oxidation. We have also recently reported the GPx activity of a series of closely related diselenides **2–4**, **34–35** using $PhSH/H_2O_2$ system [7]. Diselenides **2–4** which have quite strong Se···N interactions did not show any noticeable activity whereas diselenides **34** and **35** which have in-built coordinating amino groups but do not have Se···N interactions showed excellent peroxidase activity. The initial rate in the presence of **34** and **35** were $574{\cdot}01 \pm 23{\cdot}98$ and $466{\cdot}49 \pm 28{\cdot}26$ mM min^{-1}, respectively whereas for **1** the rate was only $28{\cdot}38 \pm 3{\cdot}88$ mM min^{-1}. The high peroxidase activity of **34** and **35** is due to the synergistic effect of two functionalities (tertiary amino and redox-active). A mechanistic study on the peroxidase activity of these diselenides shows that the nitrogen base in **34** and **35** interacts strongly with the selenium atom of selenenic acid (RSeOH) to increase the nucleophilic attack of thiol at selenium [21]. However, in contrast to the selenenyl sulphides (RSeSPh) derived from **2–4**, the ^{77}Se NMR chemical shifts of selenenyl sulphides derived from **34** and **35** reveal that these compounds do not have Se···N interaction. In these cases, the basic amino groups just deprotonate the thiol sulphydryl group to provide a high local concentration of nucleophilic thiolate anion.



30 **31** **32** NRR' = N **33** R = Me, R' = c-C_6H_{11} **34** [R,S;R,S] (+) **35** [S,R;S,R] (-)

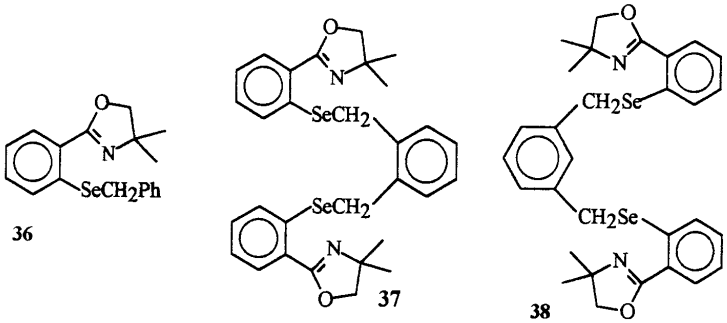
2.4 *Hybrid bi, tri and multidentate ligands*

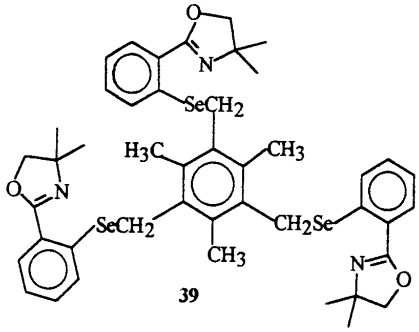
In general, aryl benzyl and aryl allyl selenides are unstable and decompose readily to give coupled hydrocarbon products and free selenium [22]. Using intramolecular coordination we have succeeded in isolating several stable aryl benzyl selenides (**36–39**) [8a]. The bidentate ligand **36** and tetradentate ligand **38** were characterized by X-ray crystallography. All attempts to synthesize the corresponding tellurium ligands were unsuccessful.

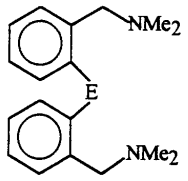
The tridentate ligands **40** and **41** were synthesized by the metathesis reactions of RLi with $Se(dtc)_2$ (dtc = diethyldithiacarbamate) and $Te(dtc)_2$, respectively [23]. The X-ray structures of **40** and **41** show that although both the nitrogen atoms interact with chalcogen atom, the Se···N interactions in **40** are found to be much weaker than the Te···N interactions in **41**. This is not surprising since the hypervalent property of divalent chalcogen increases in the order O < S < Se < Te [24]. In contrast to the synthesis of **40** and **41**, attempts to synthesize **42** and **43** by the reaction of R′Li with $Se(dtc)_2$ and $Te(dtc)_2$ were unsuccessful.

The reaction of R′Li with $Te(dtc)_2$ afforded the partially substituted tellurenyl derivative **44** instead of the expected telluride **43**. This clearly indicates that the nature of

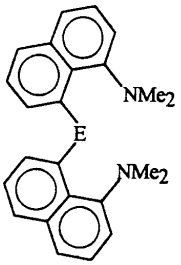
organic group affects the formation of the monotelluride. Since the ligand derived from 1-dimethylaminonapththalene is sterically bulkier than the simple 2-(dimethylamino)phenyl ligand, compounds **42** and **43** could not be isolated. Compounds **36–41** will be very useful not only as ligands for metal complexation but also as catalysts for peroxide decomposition. Studies on thiol peroxidase activity of symmetrical and unsymmetrical selenides and tellurides are in progress. The average Se···N and Te···N nonbonded interactions in **40** and **41** respectively are much weaker than those reported for the corresponding diselenide and ditelluride.



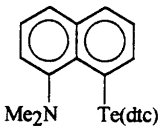




40, E = Se; **41**, E = Te



42, E = Se; **43**, E = Te



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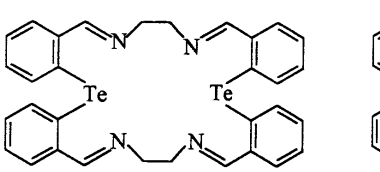
2.5 *Selenium-containing azamacrocycles*

Interest in the chemistry of macrocyclic ligands containing heavier chalcogen (Se, Te) started from the fact that the lower electronegativity combined with their greater *s* electron-donating properties of Se/Te should yield complexes with interesting structures and redox behaviour[25]. Moreover, the incorporation of the NMR active nuclei

(^{77}Se/^{125}Te) would give valuable structural information about the macrocyclic ligands and their complexes. A few years ago, our group reported an easy high yield synthesis of the novel tellurium tetraazamacrocycle **45** [26]. In order to compare the structure and coordination behaviour, some selenium-containing macrocycles have been synthesised. These ligands with 'hard' and 'soft' binding sites have the potential to coordinate to both 'hard' and 'soft' guest ions or molecules. Selenium-containing 22-, 24- and 28-membered macrocyclic Schiff base ligands (**46–48**) were synthesised via one step dipodal condensation of *bis*(o-formylphenyl)selenide and 1,2-diaminoethane, 1,3-diaminopropane and diethylenetriamine, respectively. In these cases, the secondary Se···N nonbonded interactions play an important role in the formation of a macrocyclic ring by reducing the unfavourable lone pair-lone pair repulsion between nitrogen atoms.

In contrast to the tellurium analogue, the reaction of ligand **46** with Pd(II) led to the hydrolytic cleavage of macrocycle (**49**). However, ligand **47** afforded the expected complex **50** with four nitrogen atoms coordinated to the metal ion in a square planar arrangement. It should be noted that the tellurium ligand **45** forms a novel cationic complex with palladium in which the Pd(II) ion is coordinated by two nitrogen and two tellurium atoms (**51**) [26]. Reactions of Co(II) and Ni(II) with **46** afforded the octahedral complexes **52** and **53** respectively [27].



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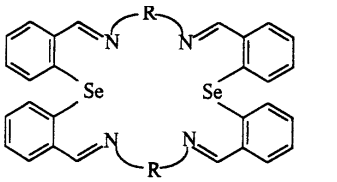
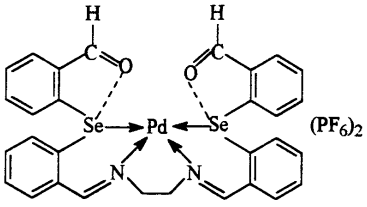


46, R = $-CH_2CH_2-$, **47**, R = $-(CH_2)_3-$
48, R = $-CH_2CH_2NHCH_2CH_2-$



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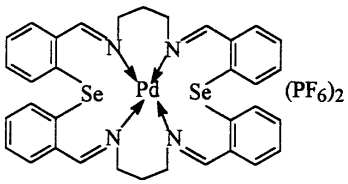

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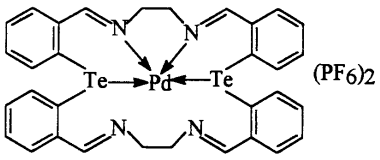

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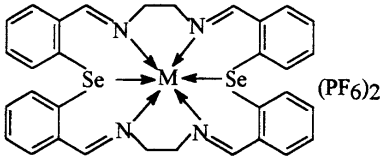

52, M = Co; **53**, M = Ni

3. Summary and conclusions

A comparison of structure and reactivity among intramolecularly coordinated organochalcogen compounds shows that the stability and reactivity of the compounds mainly depend on the strength of E···N (E = S, Se, Te) interactions. Intramolecular coordination (i) stabilizes the selenenyl halides and increases their electrophilic reactivity; (ii) stabilizes the metal chalcogenolates in monomeric form; (iii) plays an important role in the antioxidant activity of organoselenium compounds by stabilizing the intermediates such as selenol and selenenic acid; (iv) allows the isolation of stable aryl benzyl selenides and finally (v) allows the isolation of selenium and tellurium azamacrocycles without metal ion template or high dilution reaction. The use of E···N interactions in the synthesis of macrocyclic cryptants and their complexes will be reported in due course.

Acknowledgements

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