

Synthesis of sterically encumbered organoselenium species and their selectivity towards Hg(II) ions

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Received 2 March 2007; revised 24 April 2007; accepted 2 May 2007

Available online 10 May 2007

Dedicated in honor of Professor Bishan Lal Khandelwal on the occasion of his 70th birthday

Abstract—The synthesis and characterization data for an intriguing family of sterically encumbered tetrasubstituted organoselenium species are described. The open exterior geometry and flexibility of the multiple soft selenium-containing donor arms enhances conformational organization thus allowing the molecule to reveal a propensity for trapping Hg(II) ions. Preliminary studies on the ion-sensing properties of these molecules revealed that they can act as selective ionophores for Hg(II) ions.
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In continuation of our research in the area of organoselenium chemistry we became interested in designing organoselenium-based polynucleating centres in which the open coordination site of selenium can be restricted sterically by incorporating allied organic groups.¹ This work was also undertaken knowing that cyclic analogues of crown ethers and thia-crown ethers exclusively based on selenium present fairly rigid molecular structures due to intermolecular Se···Se interactions.² We also speculated that the selectivity of some of the selenium-based acyclic systems, depending on their design, might reveal unique behaviour towards guests.^{3a} The presence of selenium in the structural motif of an organochalcogen species has a significant influence on the final structure of a complex, especially with polynucleating centres, where it influences the size, shape, symmetry and orientation of the donor groups.³ The specific orientation of the donor selenium sites in a polynuclear species may also be controlled by a large number of weaker interactions, available due to heteroatoms present in allied organic groups and on selenium and thus the organochalcogens may exhibit more diverse behaviour than anticipated.⁴

If such were the case, then a study of a polynuclear system might be more rewarding as it would allow the

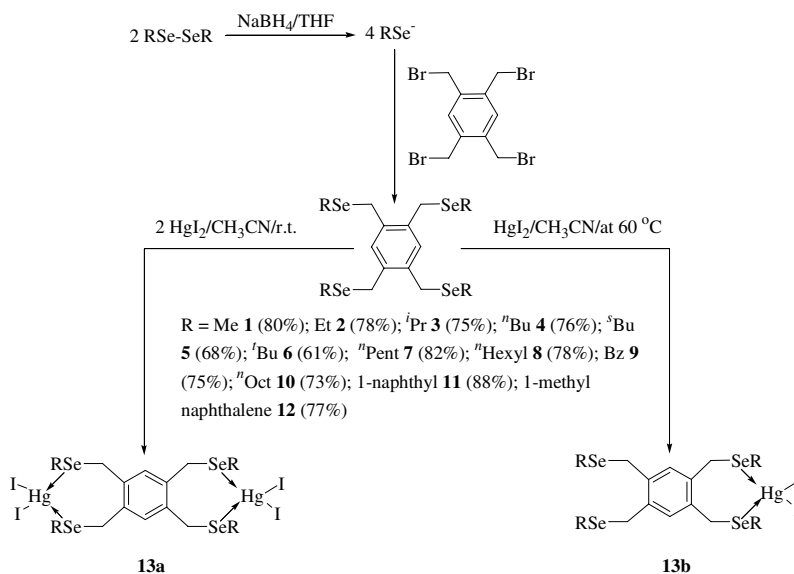
donor molecule to overcome the coordinating flexibility of soft selenium with various metal ions (without hard–soft discrimination) in a more reliable and competitive manner. This balance might lead to complementarities and high-affinity interactions especially in aliphatic selenium compounds as host molecules. Problems of insolubility, nonspecific binding or the formation of extended-reach structures, as have been frequently observed in polyarylsubstituted selenium derivatives might also be avoided.

The synthetic protocol⁵ developed to access **1–12** is outlined in **Scheme 1**. The stability of these molecules was remarkable in contrast to their simplest mononuclear alkylselenium analogues. All the compounds were characterized by elemental analysis, FAB mass, ES-MS, ¹H, ¹³C and ⁷⁷Se NMR spectroscopy.⁶

These systems have soft selenium centres and may have strong binding ability towards soft metal ions. The incorporation of selenium atoms substituted at the 1,2,4,5-positions of the central benzene ring leads to architectures which can act as suitable bridging-bidentate chelating ligands towards M²⁺ ions. The tetrakis-(*iso*-propylselenomethyl) benzene (**3**) is ineffective in coordinating metal ions such as Cr³⁺, Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, Cu⁺, Ag⁺, Zn²⁺ and Cd²⁺. Similar observations were also observed with the tetrakis-(*sec*-butylselenomethyl) benzene (**5**) moiety. The results were intriguing as coordination of these metal ions with organoselenium donors are well described in the literature.⁷

Keywords: Ion-selective electrodes; Hg²⁺ ions; Tetraalkyl-selenium; Host–guest systems.

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Scheme 1.

The receptor properties of structurally related thio-analogues with varying chain lengths and branching have also been studied with transition-metal ions by Vögtle and Weber but these analogues showed no donor–acceptor properties.⁸ These results were explained by steric crowding. Initially, we assumed that the reduced reactivity of the molecules might be due to the increased steric congestion around selenium as observed in the thio-analogues. However, we did not observe any line broadening of the benzylic $-\text{CH}_2$ signals in their respective ^1H NMR spectra. We also examined the UV–vis spectroscopic behaviour on addition of metal ions (such

as, Hg^{2+} , Cr^{3+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Cu^+ , Ag^+ , Zn^{2+} and Cd^{2+}) to a solution of species **3** or **5** and observed spectral changes only with Hg^{2+} ions as shown in Figure 1.

The complexation process caused notable changes in the absorption spectrum of **3** upon the addition of an increasing amount of Hg^{2+} ions. Addition of a solution of $\text{Ag}(\text{I})$, $\text{Pb}(\text{II})$ and $\text{Cd}(\text{II})$ ions to solutions of either **3** or **5** did not induce any change in the UV–vis spectra. Since, coordination to selenium is not an exclusive feature of mercury, the non-reactivity of species **3** with

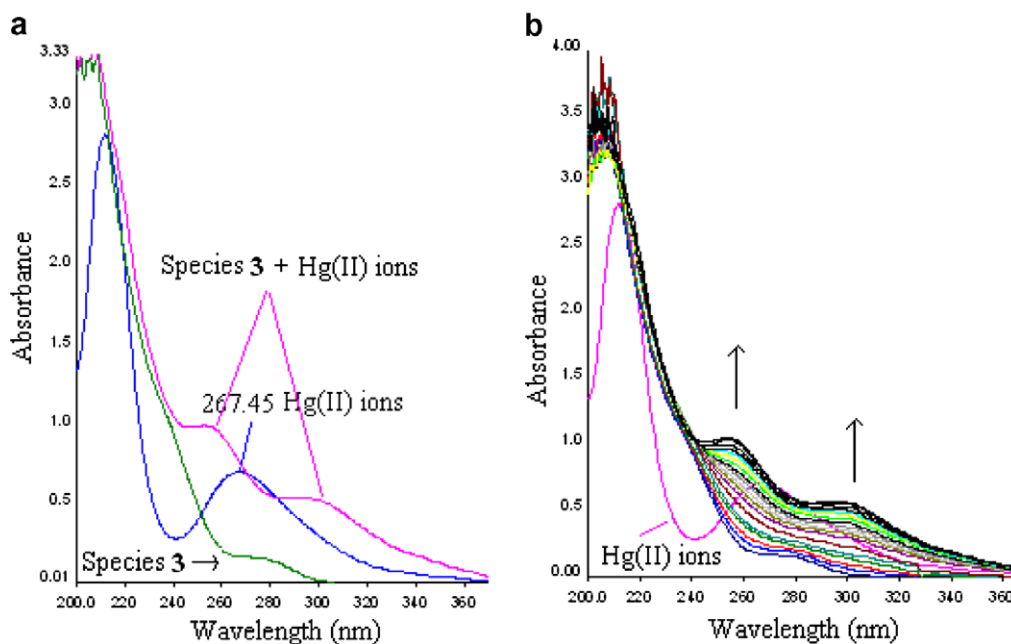


Figure 1. (a) Absorption spectra of species **3** (1×10^{-4} M, in acetonitrile), HgI_2 (1×10^{-4} M, in acetonitrile) and changes associated with the formation of a Hg-complex with species **3**. (b) The arrows show the appearance of two new bands with an increase in the absorbance on each successive addition of a solution of HgI_2 (1×10^{-3} M) in acetonitrile to a solution of species **3** (concn = 1×10^{-4} M) in acetonitrile (at almost neutral pH).

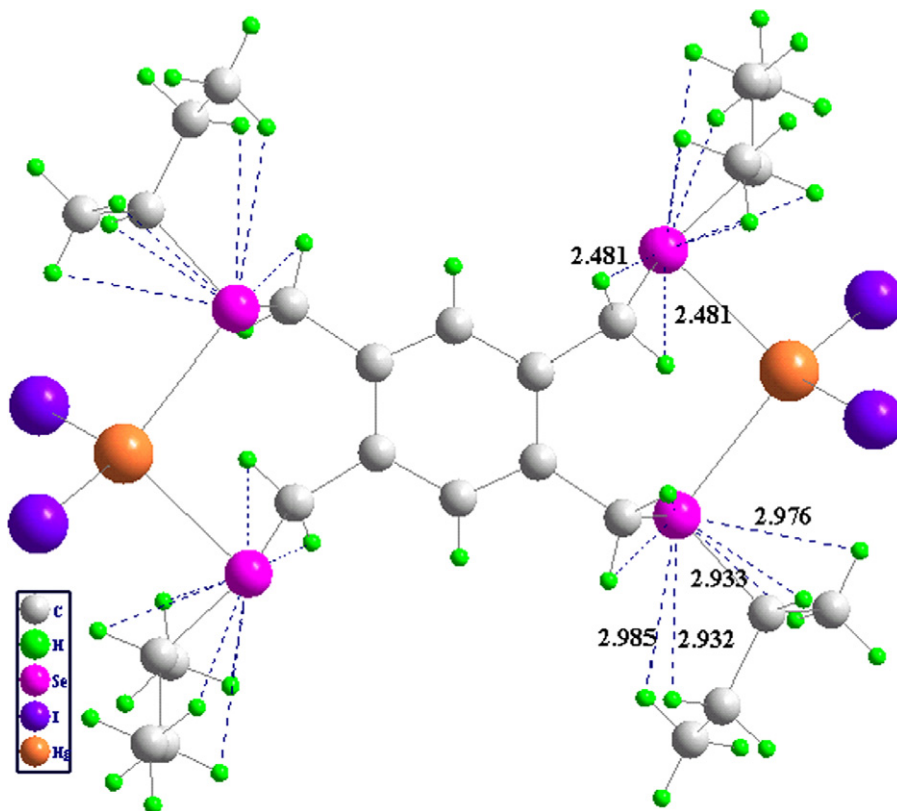


Figure 2. Perspective view of mercury complex **13a** [tetrakis(*sec*-butylselenomethyl)benzene with HgI_2] [$\text{C}_{26}\text{H}_{46}\text{Se}_4\cdot 2\text{HgI}_2$] (**13a**) showing intramolecular $\text{Se}\cdots\text{H}$ bonding.

other metal ions is strange, particularly Cu^+ , Ag^+ , Pb^{2+} and Cd^{2+} ions. The flexibility of the arms, steric bulk, open exterior geometry and multiple soft selenium donor sites make these molecules potential candidates for trapping $\text{Hg}(\text{II})$ selectively. Both a 1:1 complex and a 2:1 complex (metal–ligand) are successively formed, which is in complete agreement with physicochemical data.⁹

X-ray crystallographic study of species **13a** (Fig. 2) revealed that the $\text{Hg}\text{--}\text{Se}$ bond distances were in the range of 2.735–2.747 Å, being slightly longer than the sum of the covalent radii ($\text{Hg} + \text{Se} = 2.67$ Å). Due to the larger bite angle formed by the donor arms around $\text{Hg}(\text{II})$ in the complex ($\text{Se}\text{--}\text{Hg}\text{--}\text{Se}$ bite angle 98.30°), weaker ($\text{Hg}\text{--}\text{Se}$) coordination may be occurring. The formation of both a 1:1 complex and a 2:1 complex (metal–ligand) under two different reaction conditions suggests that $\text{Hg}(\text{II})$ ions may be labile in solution. Therefore, the stability and formation of a 1:2 complex **13a** (at room temperature) and a 1:1 complex **13b** at an elevated temperature (60°C) may be best explained due to the steric crowding and $\text{Se}\cdots\text{H}$ bonding⁴ which becomes weaker at an elevated temperature in the latter complex thus yielding complex **13b** in 1:1 stoichiometry.

Preliminary studies with ion-selective electrodes (ISEs) based on molecular species **3**, as shown in Figure 3, demonstrate that the ionophore displays a high selectivity towards Hg^{2+} over a number of other cations includ-

ing soft metal cations such as $\text{Ag}(\text{I})$ and $\text{Pb}(\text{II})$.^{10–13} The detection limit of the electrode for Hg^{2+} ions was found to be 7.94×10^{-5} M. No pH adjustments were required because the pH of pure solutions of $\text{Hg}(\text{NO}_3)_2$ lies within the functional pH range of the sensors.

In conclusion, we have described the synthesis of a family of stable tetra(alkylselenium) molecules. The examples illustrated herein suggest that there is great potential for the design of sterically encumbered organoselenium molecules to bind environmentally toxic metal ions selectively. Further investigations and

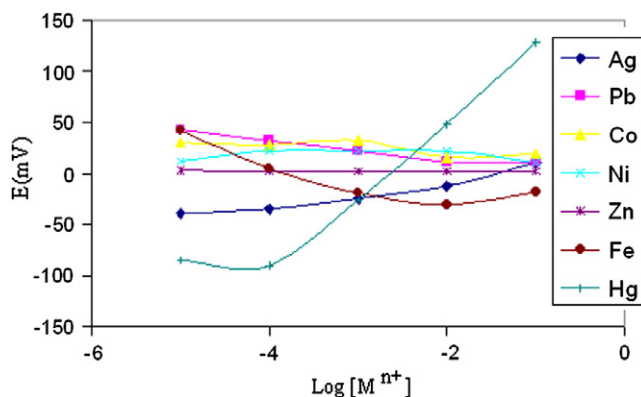


Figure 3. Response of a Hg^{2+} ion templated electrode based on species **3** and other metal ions.

elaboration of such donor architectures are currently underway in our laboratories.

Acknowledgements

The authors gratefully acknowledge the CSIR and the Department of Science and Technology (DST), Government of India for funding this study. Thanks are also due to SAIF, CDRI, Lucknow, India, for providing FAB-MS and ES-MS spectra and DST-FIST and IIT Delhi, India, for providing Single Crystal X-ray Diffraction Facilities. Special thanks to Professor A. Ramanan at IIT Delhi and Dr. K. P. Madhusudanan, Head, SAIF, CDRI, Lucknow, for their enthusiastic support in crystallographic and mass spectroscopic measurements. We also acknowledge the reviewer for his valuable comments.

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- Procedures similar to those used for arylseleno substitution were adopted and found to be equally effective and a successful strategy for alkylselenium substitution. For example, sodium alkylselenolate ions can be generated in situ by reduction of the corresponding dialkyl diselenide in aqueous THF with sodium borohydride at 0 °C. Alkylselenolate anions thus generated reacted cleanly with tetrabromomethylbenzene and, after completion of the reaction, the product in solution was recovered by conventional aqueous workup in excellent yields (>60%) and high purity. (a) Milton, M. D.; Kumar, N.; Sokhi, S. S.; Singh, S.; Singh, J. D. *Tetrahedron Lett.* **2004**, *45*, 6453–6455; (b) Kumar, N.; Milton, M. D.; Singh, J. D. *Tetrahedron Lett.* **2004**, *45*, 6611–6613.
- Physicochemical data for 3*: Light yellow solid. Yield: 75%, mp 154 °C. IR (KBr pellets): ν (cm⁻¹) = 3382, 2915, 1684, 1561, 1492, 1423, 1288. ¹H NMR (CDCl₃, 300 MHz): δ 6.93 (s, 2H, Ar), 4.26 (s, 8H, –CH₂), 3.15 (m, 4H, –CH), 1.56 (d, J = 6.4 Hz, 24H, –CH₃). Anal. Calcd for C₂₂H₃₈Se₄: C, 42.73; H, 6.19. Found: C, 42.41; H, 6.23. Compound **5**: White crystalline solid. Yield: 68%, mp 59 °C. IR (KBr pellets): ν (cm⁻¹) = 2950, 2865, 1678, 1551, 1444, 1332, 1220, 1162. ¹H NMR (CDCl₃, 300 MHz): δ 6.95 (s, 2H, Ar), 3.83 (s, 8H, –CH₂), 2.81 (m, 4H, –CH), 1.64–1.51 (m, 8H, –CH₂), 1.38 (d, J = 6.2 Hz, 12H, –CH₃), 0.92 (t, J = 6.9 Hz, 12H, –CH₃). ¹³C NMR (CDCl₃, 75 MHz): δ 134.05, 133.4, 30.6, 25.06, 23.78, 22.5, 14.03. ⁷⁷Se NMR (CDCl₃, 57.25 MHz): δ 259.5. Anal. Calcd for C₂₆H₄₆Se₄: C, 46.30; H, 6.87. Found: C, 45.98; H, 6.74. Compound **6**: Light yellow solid. Yield: 61%, mp 62 °C. IR (KBr pellets): ν (cm⁻¹) = 2949, 2854, 1687, 1557, 1449, 1457, 1363, 1155. ¹H NMR (CDCl₃, 300 MHz): δ 7.15 (s, 2H, Ar), 3.92 (s, 8H, –CH₂), 1.52 (s, 36H, –CH₃). Anal. Calcd for C₂₆H₄₆Se₄: C, 46.30; H, 6.87. Found: C, 45.46; H, 6.71.
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- Both complexes **13a** and **13b** were characterized by analytical methods. *Crystallographic data for Hg(II) complex 13a*: C₂₂H₃₈Hg₂L₄Se₄, $M = 1972.74$ g mol⁻¹, monoclinic, space group $P2_1/n$, $a = 9.476(2)$, $b = 14.651(3)$, $c = 14.746(3)$ Å, $1972.7(7)$ Å³, $Z = 2$, 14,662 reflections collected, 4747 [$R(\text{int}) = 0.0593$] independent reflections. Final $R1 = 0.0782$, and $wR2 = 0.1652$ (all data). This configuration allows the selenium atoms of the ligand to act as a bridging bidentate chelating ligand to coordinate with two mercury atoms providing a distorted tetrahedral arrangement around each mercury atom. Crystallographic data for the Hg(II) complex have been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 602915. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (+44 1223 336408; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).
- In preliminary experiments, different PVC-based ion selective membrane sensors using species **3** as ion carrier were prepared to determine the potentiometric response for different metal ions. Hg(II) ions were found to give better responses compared to other metal ions. By optimizing the conditions, the Hg(II) sensor, E1, with dioctylsebacate (DOS) as a plasticizer, gave a slope of 42.25 mV per decade over a concentration range of 1.0×10^{-1} – 1.0×10^{-4} M with an internal reference solution, 1.0×10^{-3} M Hg(NO₃)₂.
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