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Sterically encumbered hexakis(alkylseleno)benzenes: conformational behavior of hexakis(*iso*-propylselenomethyl)-benzene toward Hg^{2+} ions on selective recognition

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Abstract—An efficient synthesis and structural aspects of a novel class of hexakis(alkylseleno)benzenes $[(RSeCH_2)_6C_6]$ (R = Me, ^{i}Pr, ^{n}Bu, ^{s}Bu, ^{t}Bu, ^{n}Pn, ^{n}Hx, ^{n}Oct, 1-methylnaphthalene) by the reaction of hexakis(bromomethyl)benzene with RSe^- ions is demonstrated. Preliminary data on ion-sensing properties reveal that these species may act as selective ionophores for Hg^{2+} ions.

The importance of 1, 3, 5 versus 2, 4, 6 facial differentiation of the heteroatom bearing side chains of hexa-substituted benzenes has been well recognized in supramolecular chemistry because such molecules have shown remarkable encapsulating affinity toward metal cations, organic guest molecules,[1,2] and in the formation of coordination polymers.[3] For instance, molecular systems possessing O- and S- as subsidiary heteroatom binding groups have exhibited unique physical and chemical properties including guest inclusion and metal ion-sensing phenomena.[4]

Closely related families of other heteroatoms, such as N, P, Si, Ge, and Sn have also received considerable research on their extensive application as reagents in organic synthesis and organometallic chemistry[5,6] (Chart 1). Due to the multiple functionality, high level of substituent tunability, and conformational ordering, significant interest has been devoted toward the synthesis of such molecular systems for their applications in supramolecular chemistry as functional materials.[5] As current interest is moving toward the application of these families of compounds in chemical sciences, factors which determine the relative stability and selectivity of these different heteroatom-substituted organic molecules are likely to play further significant contributions in the intelligent design of new molecular systems.[7] As part of a more wide ranging synthetic effort to

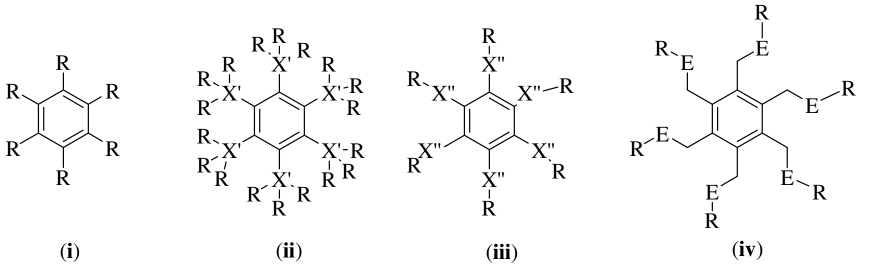

Chart 1. R = alkyl or aryl (**i**) R = alkyl or ary; X′ = C, Si, Ge or Sn (**ii**) RX″ = dialkylamino-, arylamines or heterocyclic moiety (**iii**) R = alkyl or aryl: E = O or S (**iv**).

Keywords: Hexakis(alkylseleno)benzenes; Molecular recognition; Hg^{2+} ions; Ion-selective electrodes (ISEs).

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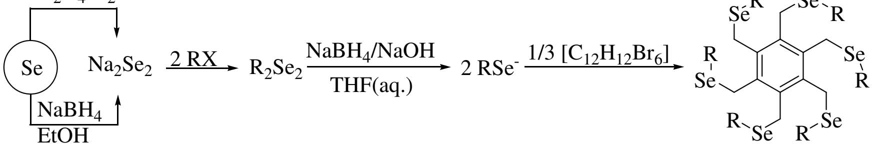
address the role of selenium in polynuclear systems[8] and in molecular recognition, we have explored the synthetic applicability of sterically-encumbered hexakis(alkylseleno)benzenes. This was undertaken knowing that the aliphatic groups may create steric encumbrance around the donor atoms depending on the alkyl groups used and they may also participate in intramolecular Se···H bonds. If such were the case, then the highly encumbered organic substituent should provide a maximum number of weak Se···H interactions. This in turn may provide additional rigidity to the molecule and controlled donor ability of selenium toward the selective guest metal ions in a differential manner moving from one molecular system to the other. Indeed, the intramolecular electronic communication may play a decisive role in controlling the specific orientation and the coordination ability of selenium to render the metal ion recognition more selective.

The reaction of hexakis(bromomethyl)benzene with a sixfold excess of aliphatic selenolate anions, generated in situ by the reaction of sodium borohydride and R_2Se_2 in aqueous THF, proceeded cleanly. Column chromatography followed by recrystallization afforded the hexakis(alkylseleno)benzenes **1**–**9** in good to high yields (Scheme 1). Hexa-substitution was exclusively observed in each case. The purity, stability, and solubility of these molecules in comparison to their aromatic analogs enabled us to examine their potential applications. Crystallographic information revealed that the alkylseleno groups in **2** prefer alternating 'up' and 'down' (1, 3, 5- vs 2, 4, 6- or *ababab*) conformations with respect to the central benzene ring.[9] As expected, each selenium center was additionally stabilized by six intramolecular Se···H interactions, four with the *iso*-propyl groups and two with the hydrogen atoms of the benzylic methylene (Se···H = 2.810–3.031 Å) which are significantly shorter than the van der Waals radius (3.20 Å).[10] Intermolecular Se···H interactions were also observed and their immediate influence can also be seen in the C–Se(4)–C bond angle, 104.8(2)°, which differs significantly from the remaining C–Se–C bond angles [99.57(18)–97.91(18)°].

On account of conformational (1, 3, 5- vs 2, 4, 6- or *ababab*) ordering[11] and assuming that the structural backbone of **2** is similar in solution, it was anticipated that this compound would offer a highly regulated reaction environment. However, we did not observe any guest inclusion as with the smaller O- and S-analogs of this hexa-host family. Our repeated attempts to isolate complexes of **2** with Fe^{3+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, Cu^{+}, Ag^{+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, and Pd^{2+} were unsuccessful and led only to the recovery of the starting materials. The structurally related S-analogs of **1**–**3** also have not shown donor–acceptor properties.[4a] The non-reactivity of the S-analogs was attributed to steric hindrance, inferred from the marked broadening of the CH_2 signal in the respective ^1H NMR spectra. We, however, did not observe broadening of the CH_2 signal in **2**.

We further examined the UV–visible spectroscopic behavior of **2** on addition of Fe^{3+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, Cu^{+}, Ag^{+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Pd^{2+}, and Hg^{2+} metal ions (1×10^{-4} mol/L, CH_3CN); significant spectral changes were observed only with Hg^{2+}. Failure of Fe^{3+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, Cu^{+}, Ag^{+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, and Pd^{2+} to interact with **2** may be due to the *ababab* conformational rigidity of the latter, which these metal ions were unable to disrupt. However, coordination of selenium is not an exclusive feature of Hg^{2+} either. It should be noted that the coordination chemistry of both non-transition and transition metal ions with monodentate or bidentate and cyclic polydentate organoselenium donors is well known in the literature.[12] Structurally, a selenium center in a molecule is far enough separated from the neighboring selenium, due to 1, 3, 5- versus 2, 4, 6- or *ababab* orientations of the donor arms, to allow multiple chelating coordination sites as observed in oxa-, thia-, and selena-crown ethers. ^1H NMR titration of **2** with soft metal ions such as Cu^{+}, Ag^{+}, Pb^{2+}, and Hg^{2+} was undertaken to ascertain the competitive coordination ability and the interactions taking place in CD_3CN solution. No significant changes in the chemical shifts were noted on addition of a molar equivalent of Cu^{+}, Ag^{+}, and Pb^{2+} ions. The expected complexes most likely form under chemical conditions with Cu^{+}, Ag^{+} and Pb^{2+} ions due to the soft nature of both the metal ion and donor selenium. However, we were able to neither crystallize nor identify these by spectroscopic means. On the contrary, the progressive addition of Hg^{2+} resulted in substantial changes in the chemical shifts. The reaction of **2** with HgI_2 in a 3:1 molar ratio at room temperature resulted in the formation of a 2:1 molecular complex **10** $[(Me_2CHSeCH_2)_6C_6]\cdot 2HgI_2$. It is apparent that conformational ordering of the host can be modulated in the presence of Hg^{2+} ions. X-ray analysis[13] of **10** (Fig. 1) revealed a new *abbabb* conformer with Hg–Se bond distances in the range of 2.761–2.805 Å, which are slightly longer than the sum of the covalent radii (Hg + Se = 2.67 Å). Under identical conditions, but at elevated temperature (60 °C), a new complex **11** $[(Me_2CHSeCH_2)_6C_6]\cdot HgI_2$ was obtained in (1:1) (ligand/metal) stoichiometry in a



Scheme 1. X = Br: R = Me **1** (88%); ^{i}Pr **2** (85%); ^{n}Bu **3** (70%); ^{s}Bu **4** (60%); ^{t}**5** (40%): ^{n}Pn 6(75%); ^{n}Hx **7** (85%); ^{n}Oct **8** (87%); 1-methylnaphthalene **9** (80%).

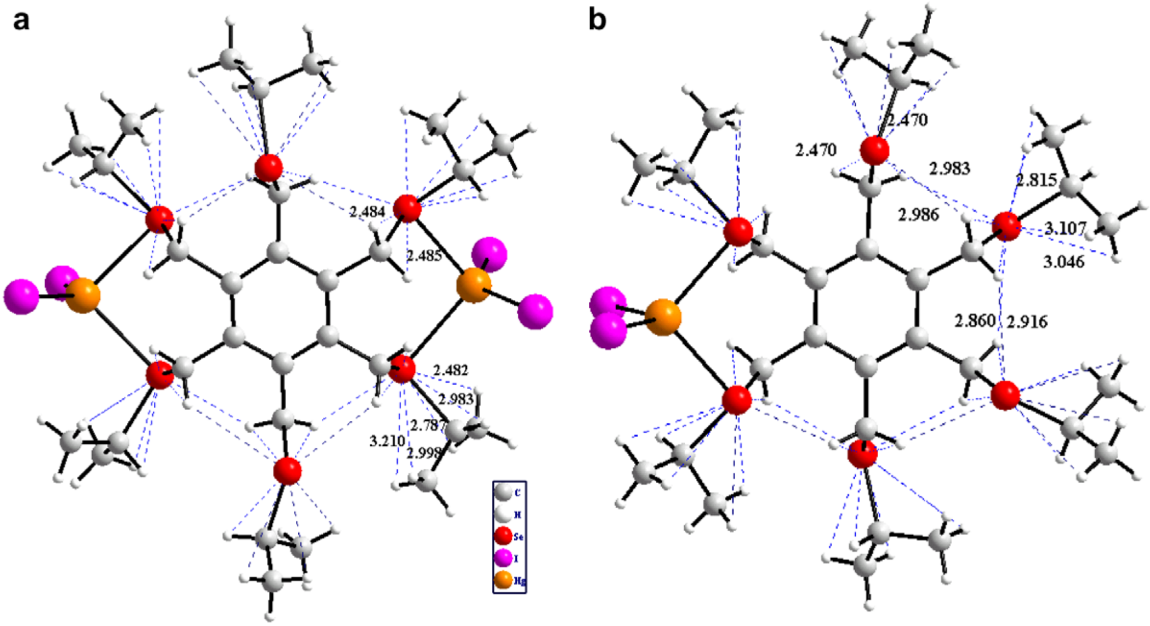


Figure 1. Perspective view of **10** $[(Me_2CHSeCH_2)_6C_6]{\cdot}2HgI_2$ (a) and **11** $[(Me_2CHSeCH_2)_6C_6]{\cdot}HgI_2$ (b) showing intramolecular Se···H interactions.

new *ababbb* conformation (Fig. 1). The coordinating selenium in both **10** and **11**, in addition to Hg–Se coordinative bonds, also shows six intramolecular Se···H interactions in the crystal structures. Four of these interactions are with the isopropyl group of the coordinating arm, as in the parent molecule **2**, and two are with the benzylic methylene of the neighboring non-coordinating arm in the range of 2.572–3.196 Å.

As has been pointed out by Gleiter et al. many short contacts between chalcogen centers and a heteroatom results in the stabilization energy being multiplied.[14] If such were the case then a slight thermal variation should release Hg^{2+} ions from the coordination site. Formation of complex **11** on heating an acetonitrile solution of **10** tentatively suggests that the intramolecular Se···H interaction stabilizes the Hg^{2+} complexes. Essentially, the influence and importance of such interactions[10] cannot be overruled in stabilizing the 2:1 complex **10**. The retainability of these interactions in solution is still under investigation and is the subject of our ongoing studies. However, the steric hindrance due to allied organic groups maintains the solid state structure in solution and the present observations support the fact that the donor selenium sites are highly influenced due to weaker (Se···H) interactions thus regulating the donor ability and the molecule behaves selectively toward Hg^{2+} ions. In the preliminary experiments to examine the properties of **2**, it was employed as an ionophore on different PVC-based ion-selective membrane sensors to determine the potentiometric responses to different metal ions. The electrode characteristics and the selectivity of PVC membrane electrodes based on **2** were established. The electrodes gave a near Nernstian slope of 33.7 mV for Hg^{2+} over a wide concentration range (1.0×10^{-1} M to 5×10^{-6} M) with a slight interference from Ag^+ at the lower detection limit in the pH range 1–4. No pH adjustment was required as the pH of a pure solution of $Hg(NO_3)_2$ lies within the above functional range of mercury-sensors.[15]

In conclusion, sterically encumbered hexaorganoselenium-substituted benzenes have been synthesized. To the best of our knowledge this is the first instance where application of a selenium-substituted hexa-host has been established in sensing Hg^{2+} ions specifically and it is hoped that our future endeavors may reveal more fundamental parameters in establishing recognition phenomena. It is interesting to note that the molecules of this category with heteroatoms such as N, O, or S have been well studied in supramolecular chemistry and are also recognized[4] as '*aromatic propellenes*', MacNicol's '*hexa-hosts*', Vögtle and Weber's '*octopus*', and Toda's '*hexa-pedals*'.

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