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ARTICLE

2,6-Dihalo-9-selenabicyclo[3.3.1]nonanes and their complexes with selenium dihalides: synthesis and structural characterisation†

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The transannular addition of $SeCl_2$ and $SeBr_2$ to cis,cis-cycloocta-1,5-diene affords 2,6-dihalo-9-selenabicyclo[3.3.1]-nonanes in high yield. The latter react with $SeCl_2$ and $SeBr_2$ to form the 2 : 1 complexes, which are the first representatives of coordination compounds with the Se···Se···Se bonds. X-ray crystallographic data of the obtained compounds are discussed. In contrast to 2,6-dihalo-9-selenabicyclo[3.3.1]nonanes, tetrahydroselenophene does not form complexes with $SeCl_2$ and $SeBr_2$ giving 1,1-dihalotetrahydroselenophenes.

Introduction

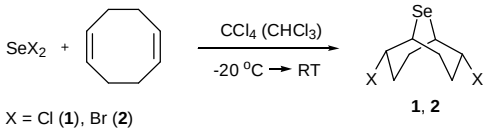
Selenium tetrachloride and tetrabromide are well known as highly electrophilic reagents, but their application in the synthesis of organoselenium compounds suffers some disadvantages. Reactions of selenium tetrahalides with unsaturated compounds often afford diorganyl selenides and products of halogenation along with the major products, diorganylselenium dihalides; the latter compounds can act as halogenation reagents toward excess unsaturated starting materials.[1] Selenium dichloride and dibromide, in contrast, are much milder Lewis acids and more selective in their chemistry. The dichloride and dibromide reagents cannot be isolated in pure form and have been studied in solution by spectroscopic methods including ^{77}Se NMR. These analyses show the dihalides to be the predominant compounds in solution, existing in equilibrium with small amounts of Se_2Cl_2 and $SeCl_4$, or $SeBr_2$ and Br_2, respectively.[2] When freshly prepared, $SeCl_2$ or $SeBr_2$ (obtained from selenium metal and sulfuryl chloride or bromine in THF, chloroform, CCl_4, or acetonitrile) can participate in reactions as pure compounds if used immediately, undergoing disproportionation more slowly if not otherwise consumed.

Little is known about complexes of the selenium dihalides other than several examples in which N-Se or S-Se bonds are made.[3-5] Complexes of selenium dichloride with tetramethylthiourea and tetrahydrothiophene were synthesized and studied by X-ray crystallography.[3] Coordination compounds with selenium and nitrogen backbones were obtained and characterized.[4] Recently complexes of selenium dihalides with organic sulfides [Me_2S, $MeS(CH_2)_2SMe$, $MeS(CH_2)_3SMe$, *o*-$(MeS)_2C_6H_4$] were described including one of selenium dibromide with tetrahydrothiophene.[5]

The organic chemistry of selenium dihalides is both intriguing and sparse.[6-9] The first synthesis of organoselenium compounds using $SeCl_2$ and $SeBr_2$ was the addition of the selenium dihalides to dimethyldiethynylsilane giving five-membered heterocycles.[6] The addition of selenium dihalides to acetylenes provided corresponding divinyl selenides.[7] Annulation reactions with selenium dihalides led to various condensed heterocyclic compounds.[8] Novel heterocycles were obtained by addition of selenium dihalides to divinyl chalcogenides.[9]

Results and Discussion

Extending our studies of the reactions of selenium dihalides with dienic compounds,[9] we explored their addition to *cis,cis*-1,5-cyclooctadiene (COD). We found that transannular addition occurs to furnish 2,6-dihalo-9-selenabicyclo[3.3.1]nonanes 1 and 2 in high yield (Scheme 1).



X = Cl (**1**), Br (**2**)

1, **2**

Scheme 1 Transannular addition of selenium dihalides to COD.

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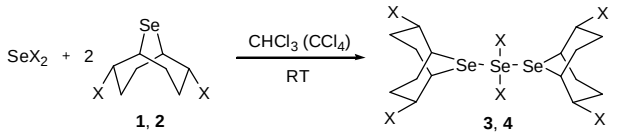
† Electronic Supplementary Information (ESI) available: crystallographic data for compounds 1-3 (CCDC 751875 – 751877).

Upon crystallization compounds 1 and 2 form unusually big crystals, which were studied by single crystal X-ray diffraction (see Supplementary Info). They represent rare examples of selenides, which have no smell and can be used as convenient ligands for coordination chemistry[10] as well as highly reactive electrophiles for organic synthesis.[11]

We found that compounds 1 and 2 react with selenium dihalides to form 2 : 1 complexes 3 and 4 in high yields (Scheme 2).

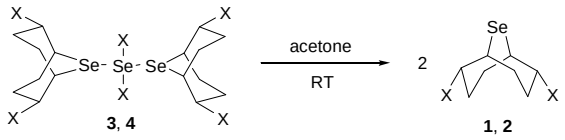


X = Cl (**1**, **3**), Br (**2**, **4**)

Scheme 2 Complexes of selenium dihalides with 1 and 2.

The order of mixing of selenium dihalides and COD was found to be important to the outcome. The highest yield of compounds 1 and 2 (94-96%) was reached by the addition of the selenium dihalide solution to COD solution in carbon tetrachloride. When the reverse order of mixing reactants was used, along with the desired compounds 1 and 2 the complexes 3 and 4 were obtained in 20-40% yield as a result of reaction of 1 and 2 with excess selenium dihalides. Chloroform is suitable solvent for preparation of complexes 3 and 4, whereas the addition of the selenium dihalides to COD proceeds more selectively in carbon tetrachloride. The formation of complexes 3 and 4 (4-8% yield) as by-products was observed when the reaction of selenium dihalides with COD was carried out in chloroform.

Complexes 3 and 4 were found to be almost insoluble in common solvents. When treated with polar solvents (acetone, DMSO) they slowly decomposed to give initial compounds 1 and 2 and presumably selenium dihalides, which underwent disproportionation. Thus, the treatment of complexes 3 and 4 with acetone led to compounds 1 and 2 in 86% and 80% yield, respectively (Scheme 3).

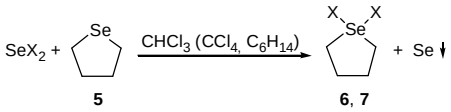


X = Cl (**1**, **3**), Br (**2**, **4**)

Scheme 3 Decomposition of complexes 3 and 4 in acetone.

Compound 1 was previously obtained from Se_2Cl_2 and COD, and characterized by IR, ^{1}H NMR, and elemental analysis.[12] Recently compound 1 and its sulfur and nitrogen analogues were used in nucleophilic substitution reactions in order to estimate a relative anchimeric assistance effect of the selenium, sulfur and nitrogen atoms by measuring the reaction rates.[11] The results obtained revealed that the anchimeric assistance effect of the selenium atom is significantly higher than those of sulfur and nitrogen atoms. That work is the first quantitative comparison of the activating abilities of these atoms in anchimeric assistance. Noteworthy, the substitution rates were largely independent of trapping nucleophiles but were strongly dependent on solvent, showing that the process is controlled by the formation of a three-membered cationic intermediate, *i.e.,* seleniranium cation in the case of compound 1.[11]

Since the complexes of $SeCl_2$ and $SeBr_2$ with tetrahydrothiophene have been described in the literature,[3,5] one can suggest that selenium dihalides could form similar complexes with the selenium analogue, tetrahydroselenophene 5. With this in mind we studied the reactions of $SeCl_2$ and $SeBr_2$ with compound 5 in a 1 : 2 molar ratio under conditions similar to those used for the preparation of complexes 3 and 4. Unfortunately, the halogenation of selenium atom in compound 5 rather than the formation of complexes took place (Scheme 4). 1,1-Dichloro- and -dibromotetrahydroselenophenes 6 and 7 were isolated in 75% and 68% yields (yields of purified compounds after recrystalization). The precipitation of red selenium was observed during the reaction. The variation of solvents ($CHCl_3$, CCl_4, hexane, etc.) did not change the course of the reaction.



X = Cl (**6**), Br (**7**)

Scheme 4 The reaction of selenium dihalides with tetrahydroselenophene.

Noteworthy, the known reaction of selenium tetrahalides with dimethyl selenide did not lead to the formation of complexes but to halogenation of selenium atom in dimethyl selenide giving dimethylselenium dihalides.[5] Cyclic selenides like tetrahydroselenophene are generally better ligands in comparison with linear selenides.[10] Nevertheless, the formation of complexes of $SeCl_2$ and $SeBr_2$ even with tetrahydroselenophene does not occur. However, the formation of complexes took place with such ligands as nonanes 1 and 2.

Previously we studied the reactions of selenium dichloride and dibromide with divinyl telluride and diallyl telluride.[13] In spite of the presence of the double bonds in these compounds, addition to the double bonds did not occur. Instead, halogenation of the tellurium atom with concomitant precipitation of elemental selenium was observed resulted in the formation of divinyl and diallyl tellurium dihalides. It is known that halophilicity increases from diorganyl selenides to diorganyl tellurides.[14] Taking into account the known data and very high halophilicity of the tellurium atom, one can suppose that the reaction of selenium dihalides with tetrahydrotellurophene will not give a complex but lead to halogenation of the tellurium atom similar to the reaction of selenium dihalides with tetrahydroselenophene (Scheme 4).

Complexes of chalcogen electron donors and electron acceptors in which there is at least partial electron transfer from donor to acceptor can be electrically conducting. Highly

conducting complexes of tetraselenafulvalene and its derivatives with acceptor compounds such as 7,7,8,8-tetracyanoquinodimethane are well known, in which the selenium atom plays the role of the electron donor.[15] In contrast, the electron-deficient selenium atom of complexes 3,4 would be an electron acceptor in potential conducting materials based on this novel motif. We therefore examined the structures of these species at the macroscopic and atomic levels.

Compounds 1, 2 and complex 3 were investigated by X-ray single crystal diffraction analysis. The complex 4 was obtained as a powder and studied by X-ray powder diffraction method.[16]

Crystals of complex 3 suitable for X-ray diffraction analysis were grown by recrystallization from chloroform. The structures of compounds 1, 2 and complex 3 were solved by direct methods and refined by the full-matrix least-squares against F^2 in anisotropic approximation for non-hydrogen atoms. The analysis of Fourier density synthesis in the crystal of compound 1 revealed disorder of all carbons atoms that can be interpreted as the superposition of two enantiomers (1:1) with all heavy atoms (Se and Cl) coinciding. Two positions of each carbon atom in the Pnma space group are interrelated by the mirror plane passing through Se1, Cl1 and Cl2 atoms. The refinement of crystal 1 in different noncentrosymmetric groups (in particular, in $Pna2_1$) or monoclinic space groups (with the account for corresponding twin law) did not change the observed static disorder. Thus, the final refinement of 1 was performed in the space group of the higher symmetry. The positions of hydrogen atoms were calculated from geometrical point of view. Crystal data and structure refinement parameters for 1, 2 and 3 are given in Supplementary Info.

The X-ray diffraction analysis (Fig. 1, Table 1) revealed 1 and 2 to be the expected derivatives of selenobicyclo[3.3.1]nonane while in 3 the latter fragment is involved in the interaction with $SeCl_2$ that interconnects bicycle fragments in a centrosymmetric structure. According to the XRD data, the compounds 1-3 crystallize as racemates in centrosymmeric space groups. The selenobicyclo[3.3.1]nonane fragment in compounds 1-3 is characterized by the chair-chair conformation with the equatorial halogen atoms. The puckering of 6-memebred cycle in 1-3 is almost the same with the deviations of C3 (C7) and Se1 atoms from the planes of the corresponding six-membered ring varying in the narrow range of 0.53-0.56 and 1.14-1.24Å. The bond lengths in bicyclic fragment are also practically independent from the nature of substituent and even from the presence of additional bonding with $SeCl_2$ in complex 3. Indeed, the Se-C bond lengths are essentially identical [1.974(3) and 1.973(3)-1.979(3)Å] in compounds 2 and 3, respectively. Some variation of Se-C bond lengths [1.952(4), 1.971(4)Å] in 1 is clearly the consequence of disorder. The C-Se-C bond angles in compounds 1, 2 and 3 are also essentially identical (Table 1). The central selenium atom in 3 is characterized by a square planar configuration with *trans*-disposition of selenium atoms of two selenobicyclo[3.3.1]nonane ligand.

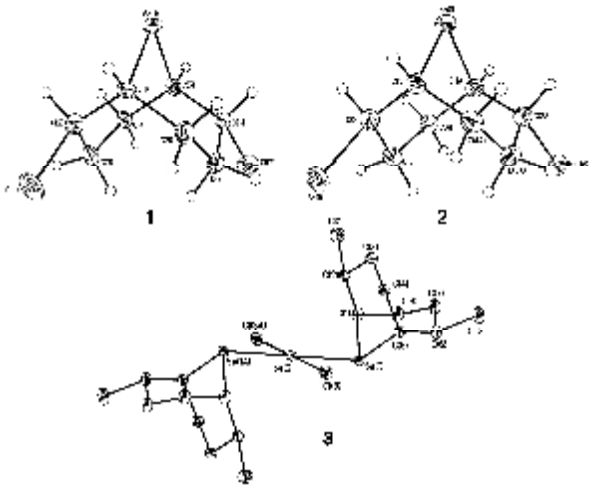


Fig. 1 X-ray crystal structures of compounds 1–3 with representation of atoms by thermal ellipsoids (p=50%) and disorder omitted for clarity. The central Se atom in 3 occupies the crystallographic center of symmetry.

Table 1 Selected bond length (Å) and angles (º) for 1, 2 and 3

	1	2	3
Se1-C1	1.952(4)	1.974(3)	1.973(3)
Se1-C5	1.971(4)	1.974(3)	1.979(3)
Se1-Se2			2.6403(3)
Se2-Cl3			2.4228(7)
C1-Se1-C5	90.85(17)	90.56(15)	90.88(11)
C2-C1-C8	118.4(3)	119.1(2)	118.8(2)
C2-C1-Se1	106.8(3)	105.05(17)	108.49(18)
C8-C1-Se1	109.2(3)	109.70(17)	106.23(18)
Cl3-Se2-Se1			89.702(18)
Cl3'-Se2-Se1			90.298(18)
Se1-Se2-Se1'			180.0
C1-Se1-Se2			105.29(8)
C5-Se1-Se2			107.64(8)
Cl3'-Se2-Cl3			180.00(3)

Comparison of structural data of complex 3 with that of the known complex of $SeCl_2$ with tetrahydrothiophene,[3] $SeCl_2(tht)_2$, indicates the similarity of the interactions of central selenium atom with sulfur and selenium atoms of the ligands. The geometry of the complex $SeCl_2(tht)_2$ is similar to 3. In particular, the Se-Cl bond lengths in 3 [2.4228(7)Å] are only slightly longer than those observed in the known complex $SeCl_2(tht)_2$ [2.4149(8)Å] and both are significantly longer than ones [2.157(3)Å] for $SeCl_2$ in gas phase.[17] Some structural differences which can be found on comparison of 3 with $SeCl_2(tht)_2$ are generally insignificant. The C-Se-Se bond angles are 105.29(8) and 107.64(8)° in 3, whereas corresponding bond angles in the complex $SeCl_2(tht)_2$ value 98.7(1) and 106.8(1)°. The Se-Se-Cl bond angles [89.702(18) and 90.298(18)°] in complex 3 are close to the average S-Se-Cl bond angle in $SeCl_2(tht)_2$ [82.70(3) and 97.30(3)° for two S-Se-Cl bond angles]. The Se···Se bonds are significantly longer than usual Se-Se bond (2.34Å) in diselenides and close to the only

available in literature dication salt of 1,11-(methanoselenomethano)-5*H*,7*H*-dibenzo[b,g][1.5]diselenocin containing the Se-Se-Se fragment [2.556-2.645(2)Å].[18]
Scanning electron microscopy of 3 and 4 revealed materials with a width varying between 50 and 1000 nm and an average length of 1-10 μm (Fig. 6S in Supplementary Info).

Conclusions

In summary, 2,6-dihalo-9-selenabicyclo[3.3.1]nonanes were obtained in high yield by the transannular addition of $SeCl_2$ and $SeBr_2$ to COD. The synthesized nonanes are promising ligands for coordination chemistry. They react with $SeCl_2$ and $SeBr_2$ to form the 2 : 1 complexes, in which three selenium atoms are arranged in a line. These are the first representatives of complexes with the Se···Se···Se coordination bonds. Establishing the possibility of forming the Se···Se···Se coordination bonds may be important for coordination chemistry and studies aiming to create conducting materials.
Compounds 1-3 were studied by single crystal X-ray crystallography. The selenobicyclo[3.3.1]nonane fragment in compounds 1-3 is characterized by the chair-chair conformation with the equatorial halogen atoms. The Se-C bond lengths and the C-Se-C bond angles are essentially identical in compounds 1, 2 and 3. Thus, the bond lengths and the bond angles in bicyclic fragment are practically independent from the nature of halogen in compounds 1 and 2 and even from the presence of additional bonding with $SeCl_2$ in complex 3. The Se···Se bonds in complex 3 are significantly longer than usual Se-Se bonds in diselenides. The central selenium atom in complex 3 is characterized by a square planar configuration with *trans*-disposition of selenium atoms of two selenobicyclo[3.3.1]nonane ligand.
The selenium variants of the 2,6-dihalobicyclo[3.3.1]nonyl core have been shown here to be easily accessible and to engage in Se···Se interactions in the solution and solid phase. Besides, the monomeric dihalides 1 and 2 are highly active in substitution reactions.[11] This chemistry occurs with anchimeric assistance from the selenium atom similar to the sulfur analogue of 1.[19]
In contrast to nonanes 1 and 2, tetrahydroselenophene does not form complexes with $SeCl_2$ and $SeBr_2$ giving 1,1-dihalotetrahydroselenophenes.

Experimental

Preparations of compounds 1-7

^1H (400.1 MHz), ^{13}C (100.6 MHz) and ^{77}Se (76.3 MHz) NMR spectra were recorded on a Bruker DPX-400 spectrometer in 5-10% solution in CCl_4 or $CDCl_3$, referenced to HMDS (^1H and ^{13}C NMR, internal) and Me_2Se (^{77}Se NMR, external). Scanning electron microscopy (SEM) study was performed on a Phillips SEM 525 M instrument. X-ray diffraction experiments were carried out with a Bruker SMART APEX II CCD area detector, using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 100 K.

Synthesis of nonane 1 by addition of selenium dichloride to COD was described in our previous work.[11] X-ray crystallographic data for 1 is shown in Supplementary Info.

2,6-Dibromo-9-selenabicyclo[3.3.1]nonane (2). Selenium dibromide (10 mmol) was prepared from elemental selenium (0.79 g, 10 mmol) and bromine (1.6 g, 10 mmol) in CCl_4 (30 mL). The solution of selenium dibromide was added dropwise to a solution of COD (1.08 g, 0.01 mol) in CCl_4 (40 mL) at -20 °C over 90 min with stirring. The mixture was stirred for 4 h at -20 °C and overnight at room temperature. Traces of the complex 4 were removed by filtration. The filtrate was evaporated to give the product 2 (3.26 g, 94% yield), which was recrystallized from CCl_4. Mp 135-136 °C. ^1H NMR (400 MHz, $CDCl_3$) *d* 2.46 (m, 4H, SeCH$\underline{CH_2}$) 2.64 (m, 2H, BrCH$\underline{CH}$), 2.97 (m, 2H, Br$\underline{CH}$CH), 3.20 (m, 2H, Se$\underline{CH}$), 5.12 (m, 2H, Br$\underline{CH}$). ^{13}C NMR (100 MHz, $CDCl_3$) *d* 32.00, 32.92, 34.86, 56.68. ^{77}Se NMR (400 MHz, $CDCl_3$) *d* 379. Found: C, 27.84; H, 3.65; Br, 45.76; Se, 22.54. Calc. for $C_8H_{12}Br_2Se$: C, 27.69; H, 3.49; Br, 46.06; Se 22.76. X-ray crystallographic data for 2 is shown in Supplementary Info.

Complex 3. Selenium dichloride (1 mmol) was prepared from elemental selenium (0.079 g, 1 mmol) and sulfuryl chloride (0.135 g, 1 mmol) and dissolved in $CHCl_3$ (10 mL). The solution of selenium dichloride was added dropwise to a solution of compound 1 (0.516 g, 2 mol) in $CHCl_3$ (50 mL) with stirring. The mixture was stirred overnight at room temperature. The precipitated powder was filtered off and the filtrate was evaporated to a volume of *ca.* 5 mL and a new portion of the precipitate was filtered off. The combined precipitate was washed with $CC1_4$ and dried to give complex 3 (0.6 g, 90% yield). The solubility of complex 3 in $CHCl_3$ was low; decomposition was observed when complex 3 was treated with polar solvents (acetone, DMSO). A crystalline sample suitable for single crystal X-ray diffraction analysis was obtained by recrystallization from chloroform. Mp 127-131 °C (decomp.). Found: C, 29.07; H, 3.78; Cl, 31.73; Se, 35.65. Calc. for $C_{16}H_{24}Cl_6Se_3$: C, 28.86; H, 3.63; Cl, 31.94; Se, 35.57. X-ray crystallographic data for 3 is shown in Supplementary Info.

Complex 4. Selenium dibromide (1 mmol) was prepared from elemental selenium (0.079 g, 1 mmol) and bromine (0.16 g, 1 mmol) in $CHCl_3$ (10 mL). The solution of selenium dibromide was added dropwise to a solution of compound 2 (0.694 g, 2 mmol) in $CHCl_3$ (50 mL) at room temperature with stirring. The mixture was stirred overnight at room temperature. The precipitated powder was filtered off and the filtrate was evaporated to a volume of *ca.* 5 mL and a new portion of the precipitate was filtered off. The combined precipitate was washed with $CC1_4$ and dried to give complex 4 (0.868 g, 93% yield). Mp 140-143 °C (decomp.). Found: C, 20.30; H, 2.69; Br, 51.25; Se, 25.27. Calc. for $C_{16}H_{24}Br_6Se_3$: C, 20.60; H, 2.59; Br, 51.40; Se, 25.40. The solubility of complex 4 in $CHCl_3$ was very low; decomposition was observed when complex 4 was treated with polar solvents (acetone, DMSO). The complex 4 was studied by X-ray powder diffraction analysis.[16]

Tetrahydroselenophene (5) was obtained in 85% yield from elemental selenium and 1,4-dibromobutane (see Supplementary Info).

1,1-Dichlorotetrahydroselenophene (6). Selenium dichloride (1.6 mmol) was prepared from elemental selenium (0.126 g, 1.6 mmol) and sulfuryl chloride (0.216 g, 1.6 mmol) and dissolved in $CHCl_3$ (4 mL). The solution of selenium dichloride was added dropwise to a solution of 5 (0.432 g, 3.2 mmol) in hexane (50 mL) at 0 °C over 10 min with stirring. The formation of red precipitate was observed. The mixture was stirred for 30 min at 0 °C and overnight at room temperature. The precipitated red powder (elemental selenium) was filtered off and the filtrate was evaporated to give crude product, which was recrystalized from CCl_4 to afford compound 6 (0.25 g, 76% yield). Mp 90-91 °C (91-92 °C, ref.[20]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.77 (m, 4H, CH_2), 4.11 (m, 4H, $SeCH_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.64 (CH_2), 64.87 ($SeCH_2$).

1,1-Dibromotetrahydroselenophene (7). The reaction was carried out by adding a chloroform solution of selenium dibromide to a CCl_4 solution of 5 under conditions similar to those of the reaction of selenium dichloride with 5. Yield of compound 7 after recrystalization from CCl_4: 68%. Mp 95-97 °C (96-98 °C, ref.[20]). ^{1}H NMR (400 MHz, $CDCl_3$) *d* 2.81 (m, 4H, CH_2), 4.12 (m, 4H, $SeCH_2$). ^{13}C NMR (100 MHz, $CDCl_3$) *d* 32.17 (CH_2), 62.86 ($SeCH_2$).

Acknowledgements

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