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Tetraselena crown ethers: synthesis and complexation with mercury salts. Crystal structure of a macrocycle and a mercury(II) complex

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Dipotassium benzene-1,2-diselenolate, $C_6H_4(SeK)_2$-1,2 obtained from the reaction of potassium *tert*-butoxide with a (benzene-1,2-diselenolato)zirconocene, was treated with $C_6H_4[SeCH_2(CH_2OCH_2)_nCH_2X]_2$-1,2 (X = Cl, $n = 1$ **1**, $n = 2$ **2**, $n = 3$ **3** or X = Br $n = 3$ **4**) leading to tetraselenacrown ethers $C_6H_4[SeCH_2(CH_2OCH_2)_nCH_2Se]_2$-$C_6H_4$ ($n = 1$ **6**, $n = 2$ **7** or $n = 3$ **8**) in a moderate yield (10–20%). This yield can be increased by using the 'caesium effect' from benzene-1,2-diselenol (18–40%). These macrocyclic compounds are able to complex heavy metals [especially mercury(II) ions] *via* their selenium atoms. The mercury complexes have been characterized by multinuclear NMR spectroscopy. The molecular structures of the tetraselenacrown ether **7** and the mercury complex of macrocycle **8** have been established by X-ray diffraction.

The first synthesis of macrocyclic polyethers was described by Pedersen[1] several years ago. He had also discovered that crown ethers are able to form complexes with alkali metals and alkaline-earth-metal cations. The chemistry of other macrocycles bearing nitrogen or sulfur atoms has also been largely developed.[2] These compounds, as well as those containing different heteroelements (phosphorus–oxygen, –sulfur or –nitrogen), usually show a great affinity for transition-metal cations.[3] In the field of systems bearing heavy chalcogens, selena- and tellura-ethers exhibit a rich co-ordination chemistry.[4] However, in general, macrocyclic ligands exhibit different co-ordination properties compared to their acyclic counterparts.[5] In parallel to our preliminary work[6] concerning diselenacrown ethers, a few examples have been recently described[7] and some of their complexes synthesized.[8]

Only recently, ligands able to complex two or more different metal cations, such as transition metal and alkali metal or alkaline-earth-metal cations, in close proximity have been reported.[9] It was anticipated that co-complexation of a hard cation and a transition-metal cation in the same macrocycle would change the redox properties of the transition-metal cation. Such complexes may be used for bimetallic catalysis, activation and formation of supramolecular systems.[9]

We have initiated a study on the synthesis of tetraselenacrown ethers incorporating several oxygen atoms in the bridge and we report herein the results concerning macrocycles of three different sizes. Preliminary reports on this work have already been presented at two international conferences in the fields of organometallic and co-ordination chemistry.[10] The syntheses of these selenacrown ethers from polybenzene-1,2-diselenol) were published by Xu and co-workers[11] during the writing of our paper, but only poor spectroscopic characterizations of the selena macrocycles were given. We report herein the syntheses of tetraselenacrown ethers from (benzene-1,2-diselenolato)zirconocene. Multinuclear NMR and mass spectrometry determinations have also been carried out. The complexation of these crown selenoethers has been achieved by their reaction with mercury(II) iodide. Crystal structures of one macrocycle and one mercury(II) adduct are reported.

Experimental

General procedures

All manipulations were carried out under an argon atmosphere using conventional Schlenk techniques. Solvents were of reagent grade and were purified by distillation from sodium–benzophenone under an argon atmosphere prior to use. The NMR spectra were recorded using a Bruker AC200 spectrometer operating at 200.13 MHz for proton and 50.30 MHz for carbon, the chemical shifts being reported relative to $SiMe_4$ used as an external reference. The ^{77}Se NMR spectra were recorded at 95.30 MHz using a Bruker DRX500 spectrometer, the chemical shifts being given relative to Me_2Se; spectra were recorded in decoupling mode using 32K data points and free induction decays were zero filled to 64K giving a final resolution of about 0.1 Hz. Mass spectra were carried out on Finnigan 3300 or Kratos VG 30F (electronic ionization 70 eV $\approx 1.121 \times 10^{-17}$ J) spectrometers. Elemental analyses were performed by the 'Laboratoire central d'analyse du CNRS', Vernaison, France.

The (benzene-1,2-diselenolato)zirconocene and dipotassium benzene-1,2-diselenolate were obtained according to previously reported procedures.[12,13] The (3-methoxybenzene-1,2-diselenolato)zirconocene **12** was prepared by literature methods.[14] The chloroethers used in the synthesis were commercial products, distilled before use. Since the preparations of compounds **1**–**4** are essentially identical only the experimental details for **1** are presented. For the preparation of compounds **6**–**8** two methods will be described. Compounds **15**–**17** were synthesized in a similar way with the appropriate macrocycle, thus only one preparation is described.

Synthesis of the dihalogeno selenoethers

$C_6H_4(SeCH_2CH_2OCH_2CH_2Cl)_2$-1,2 1. To $C_6H_4(SeK)_2$-1,2 (0.850 g, 2.72 mmol) in tetrahydrofuran (thf) (30 cm^3) preheated to reflux was added *via* a cannula $(ClCH_2CH_2)_2O$ (0.78 g, 5.45 mmol) in thf (25 cm^3). With stirring the reaction mixture was then refluxed overnight, cooled to room temperature and the solvent was removed *in vacuo* to yield a coloured oil. The residue was flash-chromatographed (eluents: pentane and then pentane–diethyl ether), affording the product **1** (oil). Yield: 0.366 g, 30%. NMR ($CDCl_3$, 25 °C): ^1H (200 MHz), δ 7.41 (dd, 2 H), 7.15 (dd, 2 H), 3.68 (m, 12 H) and 3.05 (t, 4 H); ^{77}Se (57.24 MHz), δ 264. Mass spectrum: *m/z* 450 (M^+, 14), 343 ($M - CH_2CH_2OCH_2CH_2Cl$, 13) and 236 ($C_6H_4Se_2^+$, 80%).

$C_6H_4(SeCH_2CH_2OCH_2CH_2OCH_2CH_2Cl)_2$-1,2 2. The procedure employed for the synthesis of **2** is identical to that for **1**

using the halogeno ether $(CH_2OCH_2CH_2Cl)_2$. Yield: 0.263 g, 18%. NMR ($CDCl_3$, 25 °C): ^1H (200 MHz), δ 7.38 (dd, 2 H), 7.12 (dd, 2 H), 3.66 (m, 20 H) and 3.05 (t, 4 H); ^{77}Se (57.24 MHz), δ 263. Mass spectrum: *m/z* 538 (M^+, 15), 387 [$M - (CH_2CH_2O)_2CH_2CH_2Cl$, 12] and 236 ($C_6H_4Se_2^+$, 24%).

$C_6H_4[SeCH_2CH_2(OCH_2CH_2)_2OCH_2CH_2X]_2$-1,2 (X = Cl 3 or Br 4). The synthesis of **3** and **4** was performed as for **1** with the appropriate halogeno ether, $(ClCH_2CH_2OCH_2CH_2)_2O$ and $(BrCH_2CH_2OCH_2CH_2)_2O$, respectively.

3 Yield: 0.255 g, 15%. NMR ($CDCl_3$, 25 °C): ^1H (200 MHz), δ 7.39 (dd, 2 H), 7.13 (dd, 2 H), 3.79 (t, 4 H), 3.73 (t, 4 H), 3.63 (m, 16 H), 3.55 (t, 4 H), 3.06 (t, 4 H); ^{77}Se (57.24 MHz), δ 263. Mass spectrum: *m/z* 626 (M^+, 20), 431 [$M - (CH_2CH_2O)_3CH_2CH_2Cl$, 20] and 236 ($C_6H_4Se_2^+$, 24%).

4 Yield: 0.253 g, 13%. NMR ($CDCl_3$, 25 °C): ^1H (200 MHz), δ 7.39 (dd, 2 H), 7.14 (dd, 2 H), 3.80 (t, 4 H), 3.74 (t, 4 H), 3.64 (m, 16 H), 3.46 (t, 4 H) and 3.07 (t, 4 H); ^{77}Se (57.24 MHz), δ 262. Mass spectrum: *m/z* 714 (M^+, 30), 475 [$M - (CH_2CH_2O)_3CH_2CH_2Br$, 11] and 236 ($C_6H_4Se_2^+$, 29%).

Synthesis of the tetraselena macrocycles

Method (*i*). To thf (170 cm^3) preheated to reflux were slowly added over 8 h a solution of dichloroselenoether **1**–**3** (1.27 mmol) in thf (20 cm^3) and a solution of dipotassium benzene-1,2-diselenolate **5** (0.39 g, 1.27 mmol) in thf (20 cm^3). The reaction mixture was refluxed for 12 h. The solvent was removed *in vacuo* and the residue obtained was purified by flash chromatography on a silica gel column eluted with pentane–diethyl ether.

Method (*ii*). Under argon, a solution of the (benzene-1,2-diselenolato)zirconocene **9** (0.57 g, 1 mmol) in thf (25 cm^3) was treated at room temperature with a solution of HCl gas in thf until the solution became colourless. After removal of the solvent, the residue was extracted with pentane (20 cm^3) then filtered. The solvent was evaporated under vacuum, the benzene-1,2-diselenol **10** (0.24 g, 1 mmol) thus obtained was dissolved in methanol (50 cm^3) and caesium carbonate (0.33 g, 1 mmol) was added. When the caesium carbonate was completely dissolved, the methanol was removed and dimethylformamide (dmf) (5 cm^3) and then the dichloroselenoether **1**–**3** (1 mmol) were added. The final suspension was stirred at 65 °C for 4 d. The solvent was removed *in vacuo* and the residue was dissolved in CH_2Cl_2 (20 cm^3) and a solution of KOH (20 cm^3, 10%). The organic layer was washed twice with KOH solution (20 cm^3, 1%) then dried over $MgSO_4$. After the removal of the solvent the residue was purified by flash chromatography (silica, eluent: pentane–diethyl ether).

The macrocycle **14** has been synthesized following method (*ii*), starting from complex **12** (0.599 g, 1 mmol).

6 Yield: 0.06 g, 10% (*i*); 0.11 g, 18% (*ii*) (Found: C, 39.50; H, 3.85. $C_{20}H_{24}O_2Se_4$ requires C, 39.20; H, 3.90%), m.p. 139 °C. NMR ($CDCl_3$, 25 °C): ^1H (200 MHz), δ 7.38 (dd, 4 H), 7.10 (dd, 4 H), 3.76 (t, 8 H) and 3.03 (t, 8 H); ^{13}C-{^1H} (50.3 MHz), δ 135.0, 132.8, 127.6, 70 and 27.6; ^{77}Se (57.24 MHz), δ 278. Mass spectrum: *m/z* 610 (M^+, 30) and 236 ($C_6H_4Se_2^+$, 75%).

7 Yield: 0.13 g, 18% (*i*); 0.18 g, 25% (*ii*) (Found: C, 41.45; H, 4.50. $C_{24}H_{32}O_4Se_4$ requires C, 41.15; H, 4.55%), m.p. 109 °C. NMR ($CDCl_3$, 25 °C): ^1H (200 MHz), δ 7.39 (dd, 4 H), 7.10 (dd, 4 H), 3.77 (t, 8 H), 3.59 (s, 8 H) and 3.06 (t, 8 H); ^{13}C-{^1H} (50.3 MHz), δ 134.8, 132.0, 127.4, 70.5 and 27.4; ^{77}Se (57.24 MHz), δ 268. Mass spectrum: *m/z* 700 (M^+, 20) and 236 ($C_6H_4Se_2^+$, 100%).

8 Yield: 0.20 g, 25% (*i*); 0.32 g, 40% (*ii*) (Found: C, 42.95; H, 5.00. $C_{28}H_{40}O_6Se_4$ requires C, 42.65; H, 5.10%), m.p. 93 °C. NMR ($CDCl_3$, 25 °C): ^1H (200 MHz), δ 7.38 (dd, 4 H), 7.10 (dd, 4 H), 3.74 (t, 8 H), 3.60 (s, 20 H) and 3.05 (t, 8 H); ^{13}C-{^1H} (50.3 MHz), δ 134.6, 132.0, 127.4, 70.5 and 27.0; ^{77}Se (57.24 MHz), δ 265. Mass spectrum: *m/z* 788 (M^+, 20%).

10 Quantitative yield. NMR ($CDCl_3$, 25 °C): ^1H (200 MHz), δ 7.50 (dd, 2 H), 7.04 (dd, 2 H) and 2.01 (s, 2 H). Mass spectrum: *m/z* 236 ($M^+ - 2$, 48%).

14 Yield: 0.16 g, 22% (*ii*) (Found: C, 41.45; H, 4.85. $C_{25}H_{34}O_5Se_4$ requires C, 41.10; H, 4.65%), m.p. 88 °C. NMR ($CDCl_3$, 25 °C): ^1H (200 MHz), δ 7.41 (dd, 2 H), 7.18 (t, 1 H), 7.11 (dd, 2 H), 6.85 (dd, 1 H), 6.66 (dd, 1 H), 3.74 (m, 8 H), 3.59 (s, 8 H), 3.39 (s, 3 H) and 3.05 (m, 8 H); ^{13}C-{^1H} (50.3 MHz), δ 135.0, 132.5, 130.3, 127.4, 119.8, 107.7, 70.5, 52.8 and 27.3; ^{77}Se (95.41 MHz), δ 286, 271, 270 and 180. Mass spectrum: *m/z* 732 (M^+, 82), 264 ($H_3COC_6H_4Se_2^+$, 88) and 236 ($C_6H_4Se_2^+$, 100%).

Synthesis of the mercury complexes

To a thf (12 cm^3) solution of the macrocycle **6**–**8** (0.108 mmol) was added dropwise at 25 °C a thf (6 cm^3) solution of HgI_2 (0.098 g, 0.216 mmol). The reaction mixture was then stirred for 40 h. The solvent was removed and the residue was recrystallized from toluene.

15 Yield: 0.112 g, 68% (Found: C, 16.05; H, 1.75. $C_{20}H_{24}Hg_2I_4O_2Se_4$ requires C, 15.80; H, 1.60%). NMR ($CDCl_3$, 25 °C): ^1H (200 MHz), δ 7.54 (dd, 4 H), 7.23 (dd, 4 H), 3.85 (t, 8 H) and 3.32 (t, 8 H); ^{13}C-{^1H} (50.3 MHz), δ 134.9, 133.6, 128.6, 69.5 and 32.0.

16 Yield: 0.124 g, 71% (Found: C, 18.15; H, 2.10. $C_{24}H_{32}Hg_2I_4O_4Se_4$ requires C, 17.90; H, 2.00%). NMR ($CDCl_3$, 25 °C): ^1H (200 MHz), δ 7.52 (dd, 4 H), 7.21 (dd, 4 H), 3.84 (t, 8 H), 3.62 (s, 8 H) and 3.27 (t, 8 H); ^{13}C-{^1H} (50.3 MHz), δ 134.8, 133.7, 128.7, 70.0 and 32.0; ^{77}Se (95.41 MHz), δ 198.5.

17 Yield: 0.15 g, 82% (Found: C, 20.10; H, 2.50. $C_{28}H_{40}Hg_2I_4O_6Se_4$ requires C, 19.80; H, 2.35%). NMR ($CDCl_3$, 25 °C): ^1H (200 MHz), δ 7.54 (dd, 4 H), 7.23 (dd, 4 H), 3.85 (t, 8 H) and 3.32 (t, 8 H); ^{13}C-{^1H} (50.3 MHz), δ 134.9, 133.6, 128.6, 69.5 and 32.0; ^{77}Se (95.41 MHz), δ 184.5.

X-Ray analyses of compounds 7 and 17

Yellow crystals of these compounds suitable for diffraction measurements were grown from CH_2Cl_2–hexane (1 : 1) (compound **7**) or toluene (compound **17**) solutions. The unit-cell determinations and data collections were carried out on an Enraf-Nonius CAD4 diffractometer. The pertinent crystallographic data are given in Table 1. All calculations were performed using the MOLEN package[15] with neutral-atom scattering factors. Intensities were corrected for Lorentz and polarization effects. A lack of systematic extinctions indicated either centrosymmetric $P\bar{1}$ or non-centrosymmetric $P1$ triclinic space group. Both structures were solved by Patterson and subsequent Fourier-difference syntheses. After isotropic refinement of the models the hydrogen atoms were placed in calculated positions, and an empirical absorption correction (DIFABS[16]) was applied for both structures. All non-hydrogen atoms were further refined with anisotropic thermal parameters. The hydrogen atoms were included in a riding model with B_{iso} fixed at $1.3B_{eq}$ for the carbon atoms bearing them. Final residuals are given in Table 1. Atomic scattering factors and anomalous dispersion coefficients were taken from the usual sources.[17]

Atomic coordinates, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/372.

Results and Discussion

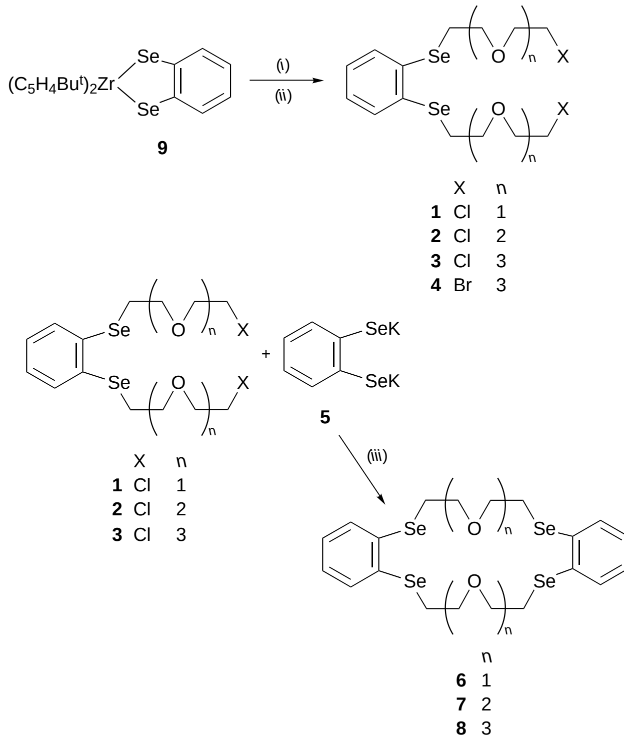
Synthesis of the tetraselena macrocycles

The tetraselenacrown ethers **6**–**8** were prepared from the dihalogeno selenoethers **1**–**4** and dipotassium benzene-1,2-diseleno-

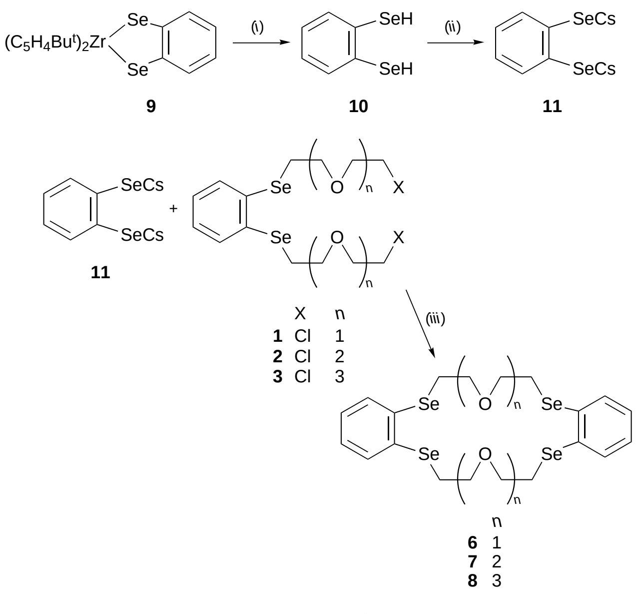
Table 1 Crystallographic data for compounds **7** and **17**

	7	**17**
Empirical formula	$C_{24}H_{32}O_4Se_4$	$C_{28}H_{40}Hg_2I_4O_6Se_4$
M	700.36	1697.26
Colour	Light yellow	Yellow
Crystal size/mm	0.2 × 0.1 × 0.1	0.2 × 0.2 × 0.15
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	7.959(2)	10.525(3)
b/Å	8.532(2)	10.885(2)
c/Å	10.628(2)	11.134(9)
α/°	85.56(2)	63.81(3)
β/°	88.27(2)	65.98(3)
γ/°	63.90(2)	86.92(2)
U/Å^3	646.2	1033.1
Z	1	1
ρ_{calc}/g cm^{-3}	1.800	2.728
F(000)	344	764
μ(Mo-Kα)/cm^{-1}	56.467	139.04
λ/Å	0.710 73	0.710 73
T/K	296(1)	296(1)
Scan type	ω–2θ	ω–2θ
Scan range/° in ω	0.9 + 0.34 tan θ	0.7 + 0.34 tan θ
hkl Range	−9 to −10, 0 to 9, 10 to 12	0 to −12, −13 to 12, 12 to 13
θ range/°	2–25	2–25
Linear decay (%)	None	None
No. of reflections	2416	3681
No. of unique reflections $I > 3\sigma(I)$	1592	2629
No. variables	145	199
Absorption correction (DIFABS)	0.7321 − 1.2317	0.6940 − 1.3314
R	0.027	0.042
R'		0.051
Weighting scheme	1	
$w = 1/\sigma(F_o)^2 = [\sigma(I)^2 + (pI)^2]^{-\frac{1}{2}}$, p		0.06
Goodness of fit	0.859	1.138
Residual density/e Å^{-3}	+0.38, −0.44	+1.24,* −0.65

* 0.98 Å from Hg.

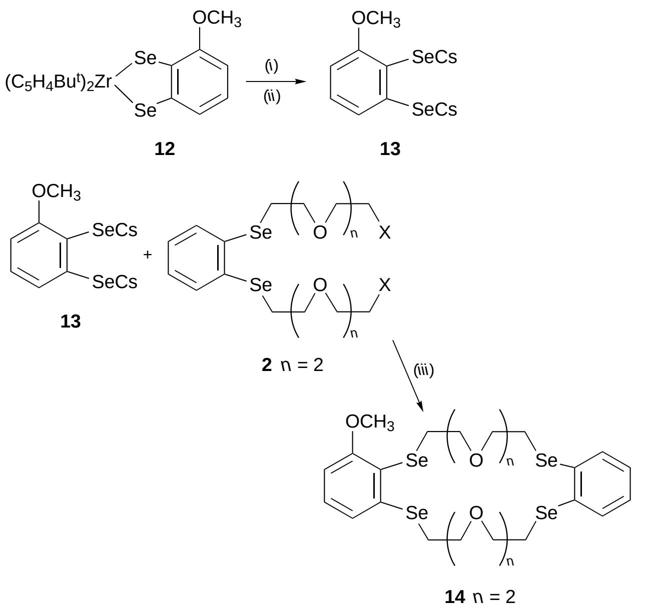


Scheme 1 (i) 2Bu^{t}OK; (ii) $2XCH_2(CH_2OCH_2)_nCH_2X$; (iii) thf, reflux



Scheme 2 (i) HCl; (ii) Cs_2CO_3; (iii) dmf

late **5** according to Scheme 1.[6,12,13] The reactions were performed using high dilution techniques and slow introduction of the reagents (pushed syringe). Following this strategy the yield increased with the length of the chain but remained quite low (10% for $n = 1$ and up to 25% for $n = 3$). However, the yield may be significantly enhanced by caesium salts, as has already been observed by several authors[18] in ring closure reactions, which often proceed without the need of high dilution techniques.[19–26] Caesium-assisted preparation of the macrocycles **6**–**8** is depicted in Scheme 2. The reaction of hydrogen chloride with the (benzene-1,2-selenolato)zirconocene **9** is fast, with a colour change from red to yellow, leading quantitatively to the benzene-1,2-diselenol **10**. Treatment of this product with



Scheme 3 (*i*) HCl; (*ii*) Cs_2CO_3; (*iii*) dmf

caesium carbonate provided quantitatively the caesium salt of the benzene-1,2-diselenolate anion **11**. Further reactions of this anion with diselenoethers **1**–**3** under mild conditions allowed the cyclization shown in Scheme 2.

Under these experimental conditions, tetraselenacrown ethers **6**–**8** have been isolated with better yields than those obtained using the potassium salt technique (up to 40% for $n = 3$). The 'caesium effect' has also been applied to the synthesis of an unsymmetrical crown ether **14** substituted on one benzene ring only (Scheme 3).

Proton, ^{13}C and ^{77}Se NMR spectroscopic data for the crown ethers **6**–**8** and **14** are given in the Experimental section.

The ^{1}H and ^{13}C NMR spectra of compounds **6**–**8** exhibit similar patterns to those previously described for diselenacrown ethers.[7]

Proton NMR spectroscopy is an efficient probe for differentiation of the crown ethers **6**–**8** from the selenoether precursors **1**–**3**. The most important differences appear mainly in the aliphatic proton region where a simplification of the crown ether spectra is shown, in particular triplets and singlets appear instead of multiplets and triplets. On the other hand, in the aromatic proton region no change occurs, two doublets of doublets (AA′XX′ system) consistent with a 1,2-disubstituted phenyl group being observed. Concerning the structure of **14**, further evidence is provided by its ^{1}H NMR spectrum: the phenyl hydrogen atoms in the positions *ortho* and *para* to the methoxy group appear as a doublet and the hydrogen atom in the *meta* position as a triplet. This distribution is in accordance with the methoxy group being at the 3 position on the benzene ring.[14]

The ^{13}C NMR spectra of macrocycles **6**–**8** are also consistent with the proposed structures: three signals appear in the aromatic region between δ 127 and 135 and two in the aliphatic region between δ 27 and 71.

Selenium-77 NMR spectroscopy provides an interesting probe for checking the stereochemistry of selenoether macrocycles with respect to the related polythio ones. In the case of crown ethers **6**–**8** only one signal is observed. These results are in accordance with a symmetrical structure. Moreover ^{77}Se NMR data showed that the selenium nuclei are slightly shielded as the length of the connecting chain increases. It seems that this chemical shift tends towards a limit for $n > 2$, when there is no more strain inside the macrocycle. On the other hand the ^{77}Se NMR spectrum of compound **14** shows four signals (δ 286, 271, 270 and 180). According to the literature we can assign the upfield signal to the selenium atom in the position *ortho* to the methoxy group.[14]

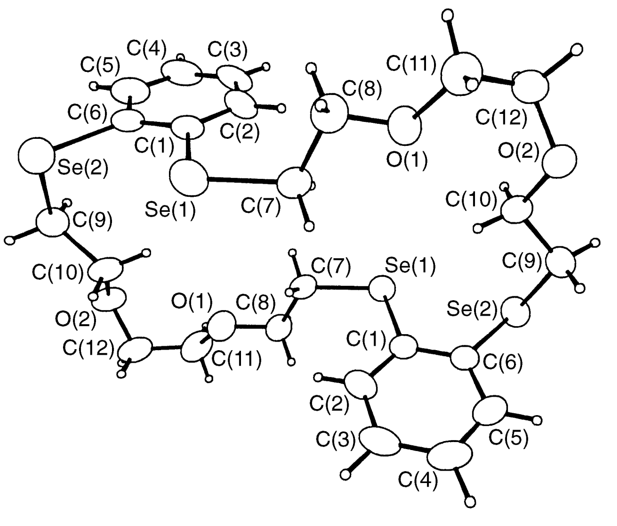
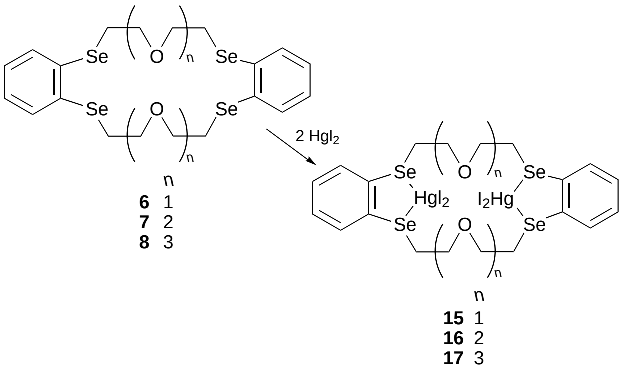


Fig. 1 The ORTEP plot (30% probability level) for compound **7**. Selected bond lengths (Å) and angles (°): Se(1)–C(1) 1.919(5), Se(1)–C(7) 1.951(4), Se(2)–C(6) 1.916(4), Se(2)–C(9) 1.956(5); C(1)–Se(1)–C(7) 100.8(2), C(6)–Se(2)–C(9) 97.1(2)



Scheme 4

The mass spectra of the macrocycles also confirm the proposed structures. In all cases the molecular isotopic pattern is in perfect accordance with the theoretical prediction as well as the successive cleavage of the two chains followed by the fragmentation of the benzodiselenide moiety shown by the peak $(C_6H_4Se_2)^+$.

The structural parameters and the conformation in the solid state of one representative macrocycle have been determined by X-ray diffraction. An ORTEP[27] drawing of the crown ether **7** is shown in Fig. 1. The molecule of macrocyclic selenoether possesses a crystallographic centre of symmetry and the metric parameters found correspond to the typical values.[28]

Complexation with mercury salts

The complexation properties of the macrocycles with transition-metal cations are governed by the polar sites in the macrocycle. Two possibilities can arise. (*i*) If there is a 'key–lock' relationship between the cation and the cavity, then the cation is located in the centre of the crown ether ring, leading to the formation of ion pairs. (*ii*) If this is not the case, the cation completely changes the conformation of the macrocycle to allow the complexation.

Consistent with the structure of the crown ethers **6**–**8**, two selenated sites (soft sites) separated by oxygenated sites (hard sites), we could expect a complexation of the second type with a modification to the conformation of the system. The reaction of macrocycles **6**–**8** with HgI_2 afforded the mercury(II) complexes **15**–**17** (Scheme 4) in good yields (68–82%).

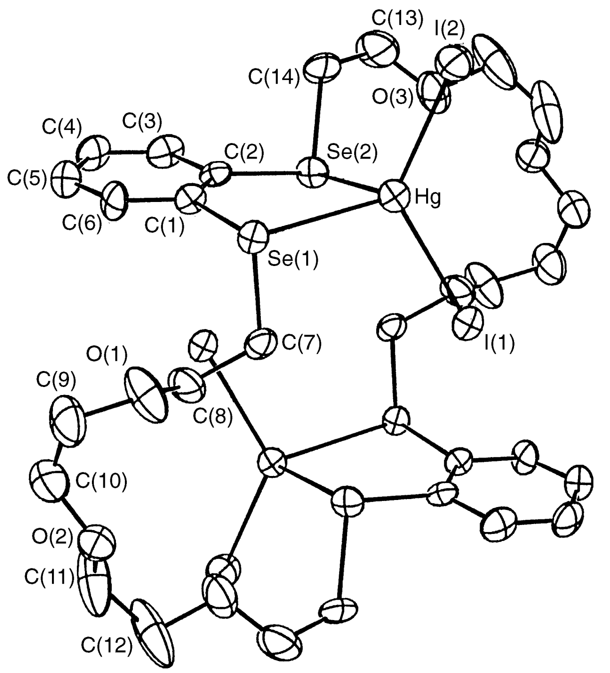


Fig. 2 The ORTEP plot (30% probability level) for compound **17**. The non-labelled atoms are related to the labelled ones by the inversion centre at 0,0,1. Selected bond lengths (Å) and angles (°): Hg–I(1) 2.672(1), Hg–I(2) 2.660(1), Hg–Se(1) 2.717(2), Hg–Se(2) 2.796(2), Se(1)–C(1) 1.90(1), Se(1)–C(7) 1.95(1), Se(2)–C(2) 1.886(8), Se(2)–C(14) 1.96(2); I(1)–Hg–I(2) 126.40(3), Se(1)–Hg–Se(2) 81.69(5), C(1)–Se(1)–C(7) 97.5(6), C(2)–Se(2)–C(14) 97.5(5)

Proton and ^{13}C NMR spectroscopic data for compounds **15**–**17** are given in the Experimental section. They are very similar to those of the macrocycles previously described. However, a very slight influence of the environment on the chemical shifts is observed. The resonances are shifted downfield in both the ^{1}H ($\Delta\delta = 0.1$ ppm) and the ^{13}C NMR spectra ($\Delta\delta = 3$–5 ppm) for the methylene group next to the selenium atom. Owing to the fact that the spectra are relatively simple, the two faces of the mercury(II) complexes are isochronous.

Selenium-77 NMR spectroscopy is potentially a powerful probe in selenium co-ordination chemistry and we report in the Experimental section the data for the synthesized complexes. The complexes are air-stable solids, very slightly soluble in chlorocarbon solvents. The spectra were obtained at 25 °C for freshly prepared saturated solutions in $CDCl_3$; the smaller the macrocycle the lower is the solubility. Complex **15** is poorly soluble in $CDCl_3$, so the ^{77}Se spectrum has not been obtained and no comparison could be made for this compound. The ^{77}Se NMR chemical shifts of the selenacrown ether complexes are usually found to higher frequency than those of the free macrocycles.[4]

The co-ordination of compounds **7** and **8** to Hg^{II} produces a large shift in δ(Se) to low frequency, in the range δ 70–81. On the one hand, this strong effect shows the great sensitivity of ^{77}Se chemical shifts to the Se environment. On the other hand, the shift to low frequency is similar to the one observed in the copper(I) complexes $[Cu\{RSe(CH_2)_nSeR\}_2]^+$ and tentatively attributed to the presence of the electron-rich d^{10} metal centre.[29]

Physical data clearly demonstrate a 2:1 metal:ligand stoichiometry and suggest that the two mercury atoms are located in the cavity of the macrocycle, close to the plane of the aromatic rings. This conclusion could not be definitive without knowing the true geometry. The structure of complex **17** has been determined by X-ray diffraction and an ORTEP drawing is shown in Fig. 2.

It is well known that mercury(II), HgX_2, molecules have a strong tendency to form linear structures which may be deformed in the solid state by secondary Hg···X interactions or by their complexation to neutral molecules. These interactions may be covalent or van der Waals in nature, thus covering the geometries from pseudo-linear to nearly tetrahedral. In mercury–selenium chemistry with four-co-ordinated Se_2HgL_2 units extreme cases have been observed: the almost linear Se–Hg–Se in mercury selenolates,[30] Cl–Hg–Cl in mercury selenanthrene[31] $[HgCl_2(C_{16}H_{16}O_4Se_2)]$ and nearly tetrahedral in mercury selenophene $[HgI_2(C_4H_8Se)_2]$.[32] The linear structures are characterized by the two short Hg–anion and the two long Hg–adduct distances. For example the Hg–Se bond lengths in the selenolate complex are close to 2.47 Å[29] while the Hg–Se distances in the selenanthrene adduct with $HgCl_2$ are equal to 3.056(4) Å. In the tetrahedral structure of the selenophene adduct with HgI_2, the Hg–Se distances are close to 2.70 Å, the Hg–I ones are close to 2.74 Å and the Se–Hg–Se and I–Hg–I angles are equal to 109.6 and 120.8° respectively. The corresponding metric parameters observed in structure **17** (Fig. 2) suggest a slight deformation from extreme tetrahedral toward linear. In fact, one Hg–Se distance is longer, the Hg–I ones are shorter, the Se–Hg–Se angle is much smaller and the I–Hg–I one larger than in the selenophene adduct with HgI_2. The differences observed may be ascribed to the presence of the chelating $Se_2C_6H_4$ ligand in complex **17**, while two monodentate selenophene ligands are present in $[HgI_2(C_4H_8Se)_2]$. There is no intermolecular interaction between HgI_2 fragments in the crystal. The shortest Hg···I intramolecular separation is 4.605(1) Å.

These mixed-donor macrocycles were designed with regard to the borderline hard/soft characteristics of the environmentally important metals. The co-ordination chemistry of the toxic heavy metal ions is of crucial importance to the design of complexing agents which may serve as sensors or extractors of the metals for biological, environmental or recycling properties.

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