DOI: 10.1002/ejic.200700837

Toward Carbohydrate Derivatives with a Markedly Acidic Centre: Structures and Reactions of Selenium(IV) Diolates

Peter Klüfers*[a] and Moritz M. Reichvilser[a]

Keywords: Selenium / Carbohydrates / Density functional calculations / X-ray diffraction / Coordination induced shift

Cyclic selenites, of the general formula (DiolH$_{-2}$)SeO, derived from the diols ethane-1,2-diol, propane-1,2-diol, *cis*-cyclopentane-1,2-diol, *cis*-cyclohexane-1,2-diol, *trans*-cyclohexane-1,2-diol, 1,1′-bicyclopentyl-1,1′-diol, 1,1′-bicyclohexyl-1,1′-diol, propane-1,3-diol, 2,2-dimethylpropane-1,3-diol, 1,1-bis(hydroxymethyl)cyclopropane, 1,1-bis(hydroxymethyl)cyclopentane, 1,4-anhydroerythritol and the methyl glycosides of β-D-ribofuranose, β-D-ribopyranose, α-D-mannopyranose, β-D-xylopyranose have been prepared and characterised by multinuclear NMR spectroscopy and single-crystal X-ray diffraction. Even with the polyfunctional sugar derivatives, oxidation of substrates did not occur. It has been demonstrated that the title compounds are hydrolytically stable at low pH values. Experimental NMR spectroscopy and structural data are consistent with results of density functional calculations and bonding has been analysed by means of natural bond orbital (NBO) theory.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2008)

Introduction

The chemistry of biomolecular chelates of the p-block elements is the subject of studies concerning interdisciplinary problems between chemistry, biology and medicine. Among the p-block elements, basic and amphoteric centres such as aluminium, gallium and bismuth(III) form hydrolytically stable classical Werner-type biomolecular chelates. An example is citrato-bismuthate, a means by which bismuth(III) may be administered as an antibiotic.[1] Biomolecular chelates of acidic centres such as silicon and phosphorus, on the other hand, are typically esters or amides which, being derivatives of inorganic acids, are intrinsically prone to hydrolysis. Examples for both types of p-block element derivatives include the most abundant class of biomolecules, the carbohydrates. Numerous carbohydrate and diol derivatives of boron,[2,3] aluminium,[4] gallium,[4] carbon,[5] silicon,[6–9] germanium,[6,10] phosphorus,[5] arsenic[5] and bismuth[5,11] have been prepared and characterised. Among these, the ester-type compounds are unstable toward hydrolysis. As an example, the tetracoordinate diol esters of orthosilicic acid rapidly hydrolyse at physiological pH, thus ruling out any significance of simple diol functions as the unknown cofactors used by silicifying organisms in the course of silica biomineralisation.[9,12] The central question thus focuses on the relationship between the properties of the acid and the hydrolytic stability of the respective carbohydrate ester. To evaluate this point, selenium(IV) was chosen as a particularly typical example of a distinctly acidic and reactive centre. In addition to the general need for a structure–properties relationship in p-block diolate chemistry, the results could be of interest to both preparative carbohydrate and medicinal chemists. The former may view the selenite function as a new kind of protective group while the latter will be able to gain a deeper insight into possible transport forms of the elements in biological systems.

The first selenious acid dialkyl ester described in literature, diethyl selenite, was prepared by Michaelis and Landmann in 1887 by the reaction of sodium ethanolate with selenyl chloride and iodoethane with silver selenite.[13] Later, the preparation of dialkyl selenites and some cyclic selenites of diols by the reaction of selenium dioxide with alcohols in aprotic solvents (benzene, dioxane, cyclohexane) was reported.[14–21] Studies concerning alkyl selenites in protic media were performed by Simon and Paetzold who showed that dimethyl selenite $(MeO)_2SeO$ is quantitatively formed upon dissolution of selenium dioxide in methanol at room temperature.[22] In the presence of other alcohols transesterification was observed,[18] whereas the reaction of dialkyl selenites, including the diol derivative ethylenedioxyselenite, both with water and alkali hydroxide solution results in rapid hydrolysis of the selenious acid esters.[19] Accordingly, all the published work on the synthesis of organyl selenites specifies to a greater (the use of $SeOCl_2$ instead of SeO_2) or lesser extent (the azeotropic removal of liberated water) the strict absence of water. The most comprehensive NMR spectroscopic study on dialkyl selenites was performed by Denney et al.[23] The structural analysis of the selenite of pinacol (2,3-dimethylbutane-2,3-diol) is the only

[a] Department Chemie und Biochemie, Ludwig-Maximilians-Universität,
Butenandtstraße 5–13 (Haus D), 81377 München, Germany
E-mail: kluef@cup.uni-muenchen.de

Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

© 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

such analysis of a dialkyl selenite described in the literature to date.[24] Moreover, all this published work deals with simple diols leaving as a challenging question whether or not there is a chemistry of the reactive selenium(IV) centre with polyfunctional biomolecules such as carbohydrates.

Results and Discussion

Preliminary experiments showed that cyclic selenites are present in considerable amounts in methanolic solution despite the predominance of the dimethyl selenite mentioned above. Figure 1 shows a ^{13}C NMR spectrum of a solution (1 M) of equimolar amounts of selenium dioxide and 1,4-anhydroerythritol in methanol. To prevent competition of alkylenedioxy and methyl ester formation, the selenites described in this work were prepared by condensation reactions between selenium dioxide and the corresponding diol or polyol in aprotic solvents (cyclohexane, dioxane). Scheme 1 gives an overview of the compounds described in this work and the corresponding numbering conventions for NMR signals. Despite the oxidising power of selenium dioxide, the preparation method proved to be more general than might have been expected. Even with carbohydrate derivatives (**13**–**16**) no oxidation of the substrate was observed.

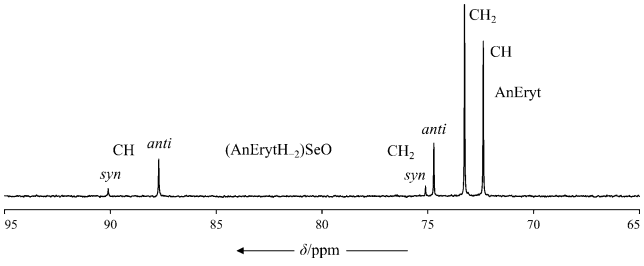
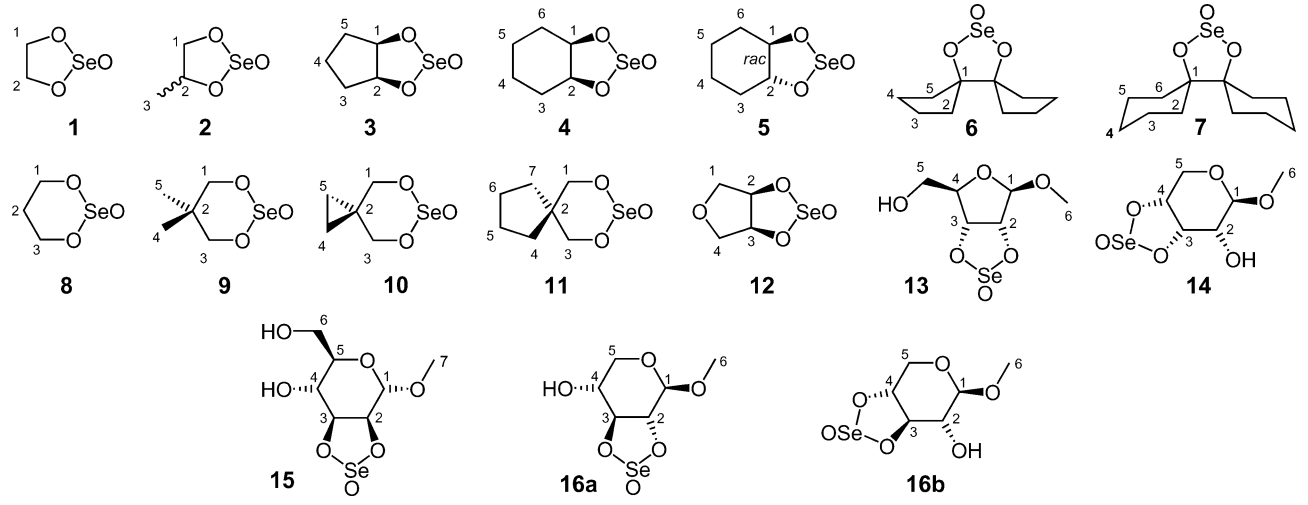


Figure 1. ^{13}C NMR spectrum of a stoichiometric mixture of 1,4-anhydroerythritol (AnEryt) and SeO_2 in methanol.

Simple Diols

The reaction of ethane-1,2-diol (Ethd) with selenium dioxide gave (EthdH$_{-2}$)SeO (**1**) as a colourless solid. In agreement with this formula, both the ^{77}Se and ^{13}C NMR spectra of the redissolved solid showed only one signal. The kinetic inertness of the diol esters on the NMR timescale can be demonstrated by using the related propane-1,2-diol as a racemic mixture. The ^{77}Se NMR spectrum showed two signals and the ^{13}C NMR spectrum showed two signal sets of different intensities. This observation is consistent with the presence of *syn*/*anti* isomerism with respect to the orientation of the substituent at the diol moiety and the oxy substituent of the selenium atom in the colourless oily mixture of (*rac*-PrpdH$_{-2}$)SeO (**2**). In addition, both *syn*- and *anti*-**2** form enantiomeric pairs since the diol was used as a racemate. Based on NMR assignments of the structurally characterised analogues of this work, *anti*-**2** can be regarded as the major product. The phenomenon of *syn*/*anti* isomerism that is well-resolved on the NMR time scale dominates the spectra of almost all the selenious acid esters reported herein. That the major product is usually the *anti* isomer was substantiated by the reaction of SeO_2 with *cis*-cyclopentane-1,2-diol (*cis*-Cptd). Again, a mixture of the *syn*- and *anti*-(*cis*-CptdH$_{-2}$)SeO (**3**) products was obtained according to NMR spectroscopy with the tentative *anti* form as the major product. Attempts to produce crystals succeeded for this diol and, in fact, structural analysis revealed the excess isomer, *anti*-**3**, as the constituent of the crystal. The molecular structure and metric parameters are depicted in Figure 2. In the crystal structure of **3**, short intermolecular O−Se dipolar contacts connect the molecules to infinite 1D chains along the crystallographic [100] direction.

Accordingly, the reaction of SeO_2 with *cis*-cyclohexane-1,2-diol (*cis*-1,2-Chxd) gave a mixture of *syn*- and *anti*-(*cis*-1,2-ChxdH$_{-2}$)SeO (**4**) as a colourless solid. The ^{77}Se NMR spectrum showed the two expected signals and the ^{13}C NMR spectrum showed two separate signal sets each of which consists of three lines. Isomers of the *syn*/*anti* type



Scheme 1. Compound numbers and atom-numbering conventions for NMR spectroscopic data.

 © 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

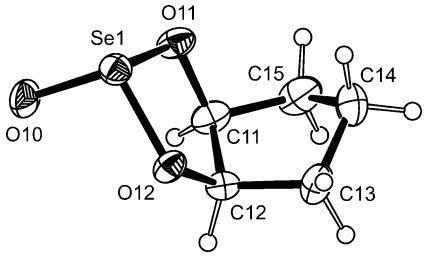


Figure 2. One of the two symmetrically independent molecules of *anti*-(*cis*-1,2-CptdH$_{-2}$)SeO in crystals of **3** (40% probability ellipsoids, hydrogen atoms with arbitrary radii). Interatomic distances [Å] and angles [°] (with standard deviations of the last digit in parentheses): Se1–O10 1.612(2), Se1–O11 1.761(2), Se1–O12 1.7712(18); O10–Se1–O11 105.51(11), O10–Se1–O12 102.24(10), O11–Se1–O12 90.41(9); O11–C11–C12–O12 20.6(3). Puckering parameters[27] of the cyclopentane ring C11–C12–C13–C14–C15: Q_2 = 0.398(4) Å, ϕ_2 = 128.1(5)°, $^{C15}T_{C14}$.

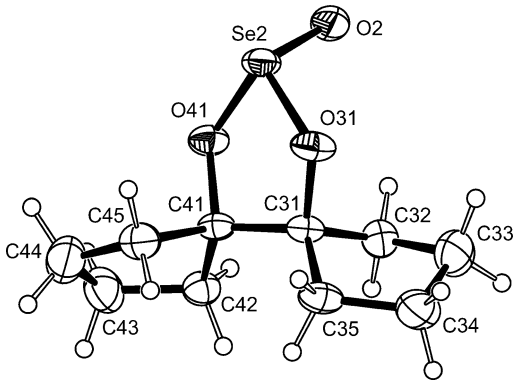


Figure 3. One of the four symmetrically independent molecules of (BptdH$_{-2}$)SeO in crystals of **6** (40% probability ellipsoids, hydrogen atoms with arbitrary radii). Interatomic distances [Å] and angles [°] (with standard deviations of the last digit in parentheses): Se2–O2 1.607(3), Se2–O31 1.784(3), Se2–O41 1.783(3); O2–Se2–O41 102.08(16), O2–Se2–O31 107.33(15), O31–Se2–O41 89.67(13); O31–C31–C41–O41 44.0(4).

are to be expected for diols that lack C_2 symmetry. Hence SeO_2 and a racemic mixture of *trans*-cyclohexane-1,2-diol (*trans*-Chxd) yielded *rac*-(*trans*-1,2-ChxdH$_{-2}$)SeO (**5**) as an enantiomeric pair. Due to the lack of *syn*/*anti* isomerism and the isochronicity of the enantiomers' signals, the ^{77}Se NMR spectrum shows one signal and the ^{13}C NMR spectrum shows one signal set consisting of six lines only. For both cyclohexane-derived diols, crystallisation has not yet succeeded.

Prior to focusing the work on carbohydrate-related substituents more bulky diols were investigated, particularly in order to study the effect of steric bulk on the oligomerisation behaviour of the oxyselenium function. Crystallisation succeeded for two bulky, C_2-symmetrical 1,2-diols: the 1,1′-bicyclopentyl-1,1′-diol (Bptd) derivative (BptdH$_{-2}$)SeO (**6**) showed the expected one ^{77}Se NMR signal and five ^{13}C NMR signals. The crystal structure contains, unusually, four symmetrically independent molecules one of which is shown in Figure 3. The other molecules adopt similar conformations with O–C–C–O torsion angles of 44–48°. The intermolecular contacts (Figure 4) generate two different types of infinite chains along the [011] axis. In the chains, both alkylenedioxy and terminal O-atoms establish dipolar contacts. The somewhat more bulky 1,1′-bicyclohexyl-1,1′-diol (Bhxd) forms the selenite (BhxdH$_{-2}$)SeO (**7**). Again, one ^{77}Se NMR signal and six ^{13}C NMR signals underline the diol's C_2 symmetry. The crystal structure contains two symmetrically independent molecules one of which is shown in Figure 5. Selenite **7** is the only compound where the intermolecular contacts do not form an infinite pattern. Instead, isolated tetramers (Figure 6), in which the selenium atoms are in a highly distorted trigonal-bipyramidal environment formed by five oxygen atoms, can be observed.

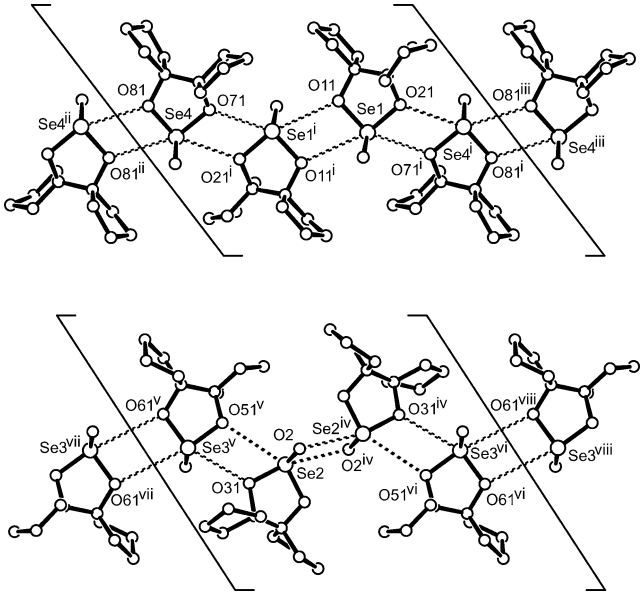


Figure 4. Two types of infinite 1D chains along the [011] direction in the crystal structure of (BptdH$_{-2}$)SeO (**6**) (atoms with arbitrary radii, hydrogen atoms are omitted for clarity). The braces represent the repetition units. Interatomic distances [Å] (with standard deviations of the last digit in parentheses): Se1–O11^{i} 3.208(3), Se1–O71^{i} 2.840(3), O21–Se4^{i} 2.898(3), O21–O71^{i} 2.687(4), Se4–O81^{ii} 2.987(3), Se2–O2^{iv} 2.955(3), Se3–O31^{v} 3.029(3), Se3–O61^{iv} 3.512(3). Symmetry codes: ^{i} $-x$, $1-y$, $1-z$; ^{ii} $-x$, $-y$, $-z$; ^{iii} x, $1+y$, $1+z$; ^{iv} $1-x$, $2-y$, $1-z$; ^{v} $1-x$, $1-y$, $1-z$; ^{vi} x, $1+y$, z; ^{vii} x, y, $z-1$; ^{viii} $1-x$, $2-y$, $2-z$.

Besides 1,2-chelation, the formation of six-membered chelate rings that incorporate a 1,3-diol function is a possible bonding pattern for a carbohydrate. In fact, simple 1,3-diols show this chelation pattern on reaction with SeO_2. Hence the parent compound propane-1,3-diol (Prpd) gave (1,3-PrpdH$_{-2}$)SeO (**8**) as a colourless solid. The ^{77}Se NMR spectrum shows one signal and the ^{13}C NMR spectrum two signals. Crystallisation succeeded with a dimethyl derivative: 2,2-dimethylpropane-1,3-diol (Dmpd) yielded (DmpdH$_{-2}$)SeO (**9**), the NMR spectra of which showed one ^{77}Se signal and four ^{13}C NMR signals. Accordingly, a crystal of **9**, an inversion twin in the polar space group *Cc* with one molecule in the asymmetric unit, consists of monomeric molecules that adopt a chair conformation with the ter-

 © 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

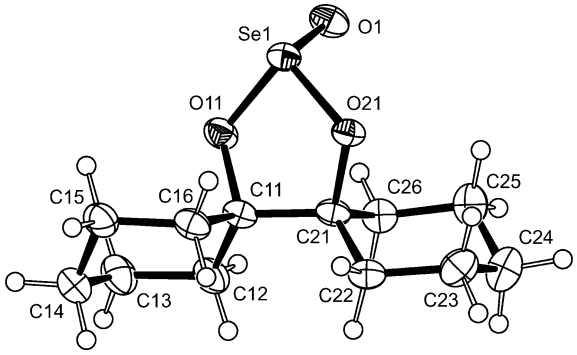


Figure 5. One of the two symmetrically independent molecules of (BhxdH$_{-2}$)SeO in crystals of **7** (50% probability ellipsoids, hydrogen atoms with arbitrary radii). Interatomic distances [Å] and angles [°] (with standard deviations of the last digit in parentheses): Se1–O1 1.6177(15), Se1–O11 1.7838(16), Se1–O21 1.7768(16); O1–Se1–O11 101.93(8), O1–Se1–O21 106.82(8), O11–Se1–O21 90.19(7); O11–C11–C21–O21 45.5(2).

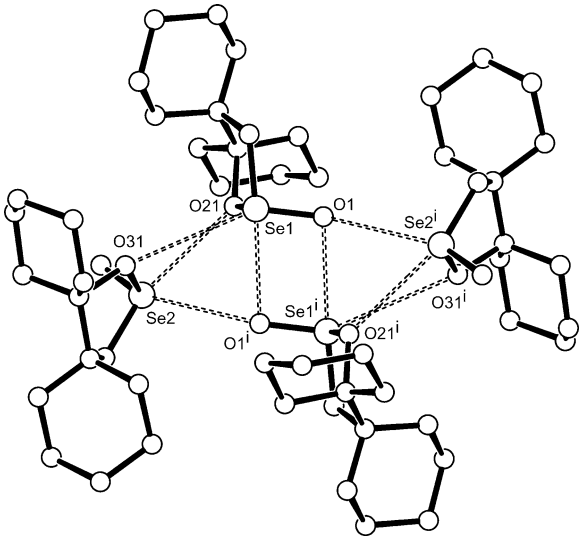


Figure 6. Isolated tetramers in the crystal structure of (BhxdH$_{-2}$)-SeO (**7**) (atoms with arbitrary radii, hydrogen atoms are omitted for clarity). Interatomic distances [Å] (with standard deviations of the last digit in parentheses): Se1–O1^{i} 2.8113(18), Se1–O31 3.4322(16), O1–Se2^{i} 3.2417(17), O21–Se2 3.0833(16), Se1–Se1^{i} 3.4443(3). Symmetry codes: ^{i} 1 – *x*, – *y*, 1 – *z*.

minal oxygen atom in an axial position (Figure 7) and slightly bent towards the inside of the six-membered ring. Dipolar contacts concatenate the molecules along the [001] axis. Structural work was possible on two more C_2-symmetric 1,3-diols and this underlines the tendency of these compounds to form chair-configured 1,3,2-dioxaselenane rings. Hence, spirocyclic derivatives were obtained by using the related 1,3-diols 1,1-bis(hydroxymethyl)cyclopropane (Bhmr) and 1,1-bis(hydroxymethyl)cyclopentane (Bhmt). The selenite (BhmrH$_{-2}$)SeO (**10**) not only shows the same number of NMR signals as **9** but also the molecular structure in crystals of **10** (Figure 8) is similar to **9** except that the cyclopropane ring distorts the tetrahedral environment at C2. Intermolecular contacts form infinite layers parallel to the [010] plane. Finally, the 1,1-bis(hydroxymethyl)cyclopentane derivative (BhmtH$_{-2}$)SeO (**11**) shows one ^{77}Se NMR signal and six ^{13}C NMR signals. The analysed crystal structure of **11** was refined as a pseudo-merohedral twin. The structure contains two symmetrically independent molecules one of which is shown in Figure 9. Again the

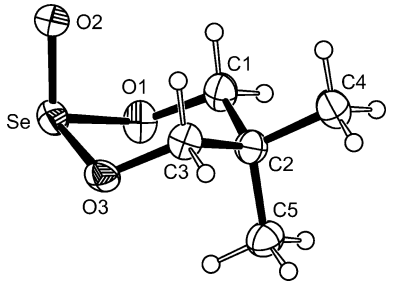


Figure 7. Structure of (DmpdH$_{-2}$)SeO in crystals of **9** (40% probability ellipsoids, hydrogen atoms with arbitrary radii). Interatomic distances [Å] and angles [°] (with standard deviations of the last digit in parentheses): Se–O2 1.611(3), Se–O1 1.768(4), Se–O3 1.775(4); O1–Se–O2 104.5(2), O2–Se–O3 104.13(18), O1–Se–O3 95.96(16).

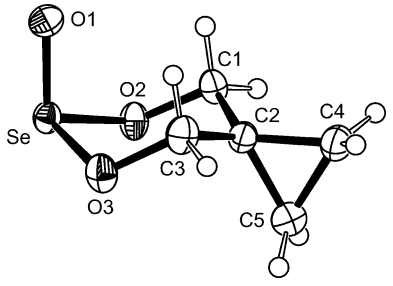


Figure 8. Structure of (BhmrH$_{-2}$)SeO in crystals of **10** (50% probability ellipsoids, hydrogen atoms with arbitrary radii). Interatomic distances [Å] and angles [°] (with standard deviations of the last digit in parentheses): Se–O1 1.614(2), Se–O2 1.788(2), Se–O3 1.799(2); O1–Se–O2 104.66(11), O1–Se–O3 102.48(11), O2–Se–O3 95.30(10).

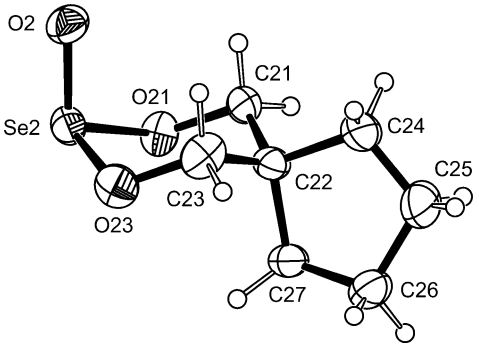


Figure 9. One of the two symmetrically independent molecules of (BhmtH$_{-2}$)SeO in crystals of **11** (40% probability ellipsoids, hydrogen atoms with arbitrary radii). Interatomic distances [Å] and angles [°] (with standard deviations of the last digit in parentheses): Se2–O2 1.602(4), Se2–O21 1.758(4), Se2–O23 1.769(4); O2–Se2–O21 105.4(2), O2–Se2–O23 104.85(19), O12–Se2–O23 95.75(16).

 © 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

conformation is similar to that of **9**. Actually, the type of intermolecular contacts is the same, that is, infinite chains along the [001] axis.

A closer approach to carbohydrates was made by using 1,4-anhydroerythritol (AnEryt) as a furanoidic 1,2-diol. Due to the lack of C_2-symmetry, *syn*/*anti* isomerism was expected. Thus surprisingly, the reaction of SeO_2 and AnEryt led to only one product, the *anti* isomer of (AnErytH$_{-2}$)SeO (**12**), according to NMR spectroscopy. The molecular structure is shown in Figure 10. The furanoidic ring adopts an envelope conformation on O4. The molecular packing is dominated by short intermolecular O−Se contacts that lead to the formation of infinite two-dimensional layers parallel to the crystallographic [001] plane.

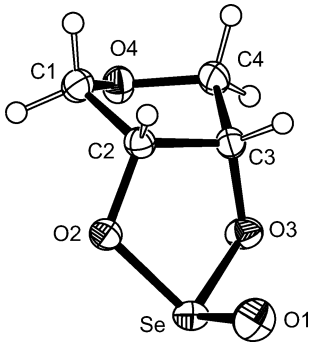


Figure 10. Structure of the *anti*-(AnErytH$_{-2}$)SeO molecules in crystals of **12** (50% probability ellipsoids, hydrogen atoms with arbitrary radii). Interatomic distances [Å] and angles [°] (with standard deviations of the last digit in parentheses): Se–O1 1.6046(16), Se–O2 1.7749(17), Se–O3 1.7781(15); O1–Se–O2 105.55(9), O1–Se–O3 104.18(8), O2–Se–O3 88.32(7); O2–C2–C3–O3 8.2(2). Puckering parameters[27] of the furanoidic ring O4–C1–C2–C3–C4: Q_2 = 0.3882(19) Å, ϕ_2 = 351.4(3)°, ^{O4}E.

Carbohydrates

The reaction of selenium dioxide and methyl β-D-ribofuranoside (Me-β-D-Rib*f*) in dioxane gave a mixture of *syn*- and *anti*-(Me-β-D-Rib*f*2,3H$_{-2}$)SeO (**13**). The mixture shows two ^{77}Se NMR signals and two ^{13}C NMR signal sets. Crystallisation succeeded and resulted in the isolation of the *anti* isomer as the major component. Figure 11 shows the molecular structure of *anti*-**13**. The isomeric molar ratio of the solutions was 3:2. The furanose ring adopts a twist conformation ($^{C1}T_{O4}$) and the CH_2OH function takes part in hydrogen bonding and is disordered. In the minor disordered component (ca. 30%, not shown in Figure 11), an intramolecular hydrogen bond from the O5 donor to the O1 acceptor is established. Instead, in the major component the O5-hydroxy group acts as a donor in intermolecular hydrogen bonding. Together with the intermolecular dipolar contacts between Se−O functions, they form an infinite 3D framework, the hydrogen-bonded part generating chains along the [100] direction.

As with the ribofuranoside, methyl β-D-ribopyranoside (Me-β-D-Rib*p*) allows the formation of either 1,2- or 1,3-diol-derived selenium compounds. However, despite this variability, the 1,2-diol-derived products *syn*- and *anti*-(Me-β-D-Rib*p*3,4H$_{-2}$)SeO (**14**) were obtained in an isomeric ratio of 3:7 (*syn*:*anti*). The ^{77}Se NMR spectrum thus shows two signals and the ^{13}C NMR spectrum shows two signal sets. Attempts to confirm this result by structural analysis led only to a preliminary X-ray analysis on crystals of poor quality. However, the assignment of a selenite group bonded to O3 and O4 instead of O2 and O3 could be clearly confirmed.

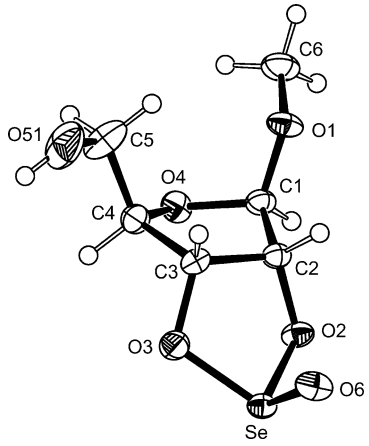


Figure 11. Structure of the *anti*-(Me-β-D-Rib*f*2,3H$_{-2}$)SeO molecules in crystals of **13** (major disorder component, 50% probability ellipsoids, hydrogen atoms with arbitrary radii). Interatomic distances [Å] and angles [°] (with standard deviations of the last digit in parentheses): Se–O6 1.6098(18), Se–O2 1.7800(18), Se–O3 1.7849(17); O2–Se–O6 103.39(9), O3–Se–O6 104.46(10), O3–Se–O2 87.55(8); O2–C2–C3–O3 8.1(3). Puckering parameters[27] of the furanose ring O4–C1–C2–C3–C4: Q_2 = 0.277(3) Å, ϕ_2 = 194.4(6)°, $^{C1}T_{O4}$.

The rules of the chelation of the divalent SeO core by a carbohydrate-derived chelator became more transparent after the reaction of two more methyl pyranosides that provide *cis*- and *trans*-1,2-diol functions as well as potential 1,3-chelators. Thus methyl α-D-mannopyranoside (Me-α-D-Man*p*) gave *syn*- and *anti*-(Me-α-D-Man*p*2,3H$_{-2}$)SeO (**15**). The ^{77}Se NMR spectrum shows two signals and the ^{13}C NMR spectrum shows two signal sets. In the case of methyl-β-D-xylopyranoside (Me-α-D-Xyl*p*) four products were obtained: *syn*- and *anti*-(Me-β-D-Xyl*p*2,3H$_{-2}$)SeO (**16a**) as well as *syn*- and *anti*-(Me-β-D-Xyl*p*3,4H$_{-2}$)SeO (**16b**). The ^{77}Se NMR spectrum shows four signals. Comparing the chemical shift values with those of the previously described compounds leads to the assumption that *anti*-**16a** and *anti*-**16b** are the predominant species.

Structural Parameters

The structures of five- and six-membered cyclic selenites throughout show Se–$O_{terminal}$ bond lengths of 1.60–1.61 Å and Se–O_{diol} bond lengths of 1.78–1.80 Å. The exocyclic O–Se–O angles are about 105°. In five-membered selenites the endocyclic O–Se–O angles are in the region of 90°, whereas in six-membered rings this angle is larger at about 96°.

 © 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Hydrolysis

Compounds such as **12** form in a methanolic solution at equilibrium with molar amounts of liberated water (Figure 1). Hence, the alkylene selenites of this work are clearly not unstable towards hydrolysis in a narrower sense. However, the title compounds are hydrolysed in pure aqueous media. Experiments were carried out with selected compounds, namely the cyclic selenites of *cis*-cyclopentane-1,2-diol (**3**), 2,2-dimethylpropane-1,3-diol (**9**), 1,4-anhydroerythritol (**12**) and methyl β-D-ribofuranoside (**13**). In all cases complete hydrolysis was observed in acidic (1 M H_2SO_4, 1 M HCl, 0.1 M HCl), neutral (pure water, no buffer) and basic (1 M and 0.1 M NaOH) aqueous media.

These findings could be partly anticipated. In neutral and basic solution, on the one hand, where resonance-stabilised selenite anions are formed, rapid and complete hydrolysis is a typical reaction of a strong acid's ester. In acidic media, on the other hand, at pH values below pK_{a1} of selenious acid H_2SeO_3 at 2.6,[25] the non-deprotonated H_2SeO_3 molecule is the competitor of the diol ester. Using the experience from coordination chemistry that a diolato complex has a good chance of being formed if this chelating dianion replaces two hydroxido ligands, the fact that complete hydrolysis was observed was not regarded as compelling. The experimental setup was thus extended to an extraction technique in order to also detect smaller equilibrium concentrations of the ester than by a direct NMR analysis.

Aqueous solutions to be extracted were prepared from SeO_2 and a molar amount of diol at a total selenium concentration of 1 mol L^{-1}. The reaction mixture was heated to 70 °C for 2 h and, after cooling, the aqueous phase was extracted with dichloromethane and the organic phase was analysed by NMR spectroscopy. As a result, the alkylene selenites derived from pinacol and anhydroerythritol were detected in the apolar solvent. By keeping the pH value sufficiently low, alkylene selenites may therefore be prepared from an aqueous solution. It remains to be investigated whether there are carbohydrate-derived diol functions that provide sufficiently high stability to the tentative chelate "complexes" to enrich the selenite ester to a higher quantity even in the aqueous solution itself.

syn/*anti*-Isomerism and Regioselectivity

Due to the high inversion barrier of the pyramidal SeO_3 group, *syn*/*anti* isomerism occurs unless the diols are C_2-symmetric. The only observed exception occurred in the case of 1,4-anhydroerythritol, where the *anti* isomer was the sole product of the reaction with selenium dioxide in boiling cyclohexane. In methanolic solution, however, both isomers were formed in equilibrium with $(MeO)_2SeO$ (Figure 1). It is unclear whether the *syn* isomer is thermodynamically less stable in the nonpolar and nonprotic solvent or whether the *anti* isomer is the kinetic product.

In the reactions of carbohydrates with equimolar amounts of selenium dioxide, the formation of six-membered selenites with 1,3-diol functions, though sterically possible, was not observed. In all cases five-membered rings formed. Since *syn*- and *anti*-**15** are the sole products of the reaction with methyl α-D-mannopyranoside, it is clear that there is a general preference for *cis*-1,2-diol groups. However, in a preliminary experiment with two equiv. of SeO_2, it was possible to obtain a six-membered selenite with esterified O4 and O6 additionally. Methyl β-D-xylopyranoside bears two vicinal *trans*-diol functions, both of which take part in the formation of selenites. Hence, the selenium(IV) atom is clearly able to participate in *trans*-pyranoidic chelate rings, an ability that silicon is lacking.[9]

The observations can be summarised as follows: in the case of furanoidic and pyranoidic diol functions, cyclic selenites are preferentially formed with *cis*-1,2-diol functions instead of 1,3-diol or pyranoidic *trans*-1,2-diol functions. The latter, however, are both able to form cyclic selenites in the absence of *cis*-1,2-diol functions.

NMR Data

Coordination induced shifts (CIS) of ^{13}C NMR signals related to the signals of the free diols together with ^{77}Se NMR chemical shifts of **1**–**14** are given in Table 1. While in selenites of 1,2-diols, the NMR signals of the α carbon atoms are invariably shifted to lower field by up to 17 ppm, the corresponding signals in derivatives of 1,3-diols gain a high-field shift of 1–4 ppm. In the case of ^{77}Se NMR spectra, one can observe the selenium signals in six-membered

Table 1. Observed (δ_{obs}) and calculated (δ_{calc}) NMR chemical shifts of the selenium and α carbon nuclei (connectivity $C_{\alpha1}$–O–Se–O–$C_{\alpha2}$). All spectra were recorded in $CDCl_3$ except that of **14** which was recorded in [D_6]DMSO. Calculated shifts are corrected according to the linear correlations given in Figures 13 and 14. The coordination induced shift (CIS) is calculated as $\delta_{product} - \delta_{diol}$. All data are given in ppm. No CIS values are given for compound **13** due to the lack of comparative data.

		^{77}Se		$^{13}C_{\alpha1}$			$^{13}C_{\alpha2}$		
		δ_{obs}	δ_{calc}	δ_{obs}	δ_{calc}	CIS	δ_{obs}	δ_{calc}	CIS
1		1430	1434	70.5	69.4	+6.7			
2	*syn*	1438	1453	74.6	74.9	+6.8	80.9	80.4	+12.6
	anti	1432	1431	75.9	75.3	+8.1	78.4	76.8	+10.1
3	*syn*	1481	1468	91.2	92.3	+17.3			
	anti	1463	1465	88.1	88.1	+14.3			
4	*syn*	1445	1440	81.0	80.7	+10.4			
	anti	1424	1438	79.7	78.7	+9.1			
5		1407	1407	87.1	85.2	+7.3	83.1	81.2	+3.3
6		1407	1412	100.8	99.3	+13.7			
7		1409	1404	92.6	90.9	+17.0			
8		1301	1300	59.1	57.2	–2.6			
9		1285	1290	68.3	66.5	–2.8			
10		1295	1294	66.5	64.5	–1.5			
11		1289	1289	67.0	65.6	–3.6			
12	*anti*	1492	1507	87.2	89.1	+15.9			
13	*syn*	1492	1495	93.4	93.3		90.0	90.4	
	anti	1481	1489	91.0	92.2		87.9	88.2	
14	*syn*	1454	1452	78.6	85.4	+7.9	76.7	78.1	+9.4
	anti	1459	1431	77.4	77.5	+6.8	75.3	75.3	+7.9

 © 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

rings in a narrow range around 1295 ppm. In five-membered rings the signals are located at 1400–1500 ppm. From the data it is evident that both the α carbon CIS values and the ^{77}Se shifts allow unambiguous assignment of whether the SeO group is coordinated by a 1,2- or a 1,3-diol functionality in polyols thus making the combined NMR spectroscopy a valuable tool for the assignment of carbohydrate bonding modes towards selenium(IV).

DFT Calculations

Geometrical Parameters

Structural optimisations were performed at the B3LYP/6-31+G(2d,p) level of theory for **1**–**14**. Theoretically derived bond lengths and O–Se–O angles are practically identical to the experimental data from the X-ray structure analyses. The only significant differences concern the O–C–C–O torsion angles in **3** and **12**. While the X-ray structures show torsion angles of up to about 20°, the calculations (although symmetry was turned off) predict almost perfect planarity. As can be seen from an energy profile of the O–C–C–O torsion in **3** (Figure 12), the total energy in the gas phase depends only slightly on the actual torsion angle. Hence, it can be assumed that the angle in the solid state adjusts so that an optimisation of (basically dipolar) intermolecular contacts is achieved.

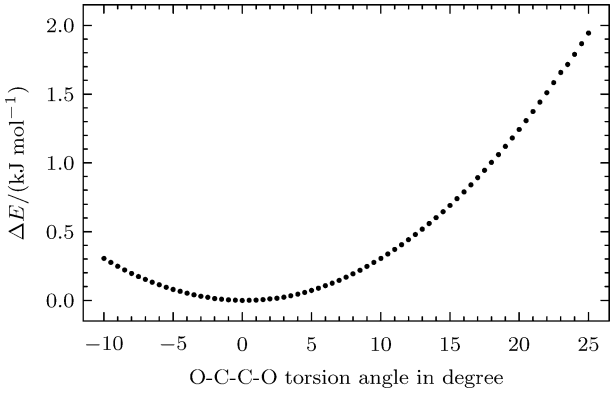


Figure 12. Total energy [B3LYP/6-31+G(2d,p), with an ultra-fine integration grid and very tight convergence criteria] of *anti*-(*cis*-1,2-CptdH$_{-2}$)SeO (**3**) as a function of the O–C–C–O torsion angle.

NMR Data

NMR chemical shift calculations were performed at the PBE1PBE/6-311++G(2d,p) level of theory on the B3LYP/6-31+G(2d,p)-optimised structures and referenced to Me_4Si and Me_2Se data which were calculated by the same method. The shift values of nuclei which are symmetrically equivalent in solution were averaged. Figure 13 shows the correlation between calculated and observed ^{13}C NMR chemical shifts for **1**–**14**. The linear dependence is best described by the following equation.

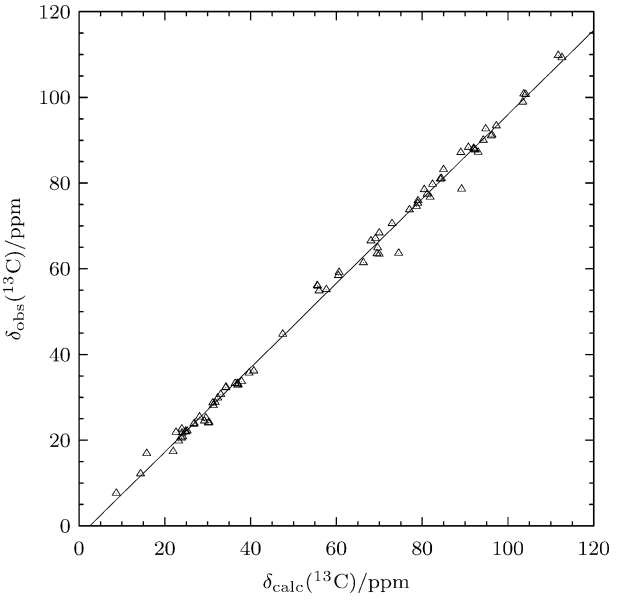


Figure 13. Linear correlation between calculated [δ_{calc}, PBE1PBE/6-311++G(2d,p)] and observed (δ_{obs}) ^{13}C NMR chemical shifts. Included are data of compounds **1**–**14** (both *syn*- and *anti*-isomer if existent). The correlation is described by the linear equation $\delta_{obs}(^{13}C)/ppm = 0.984(7) \cdot \delta_{calc}(^{13}C)/ppm - 2.4(5)$.

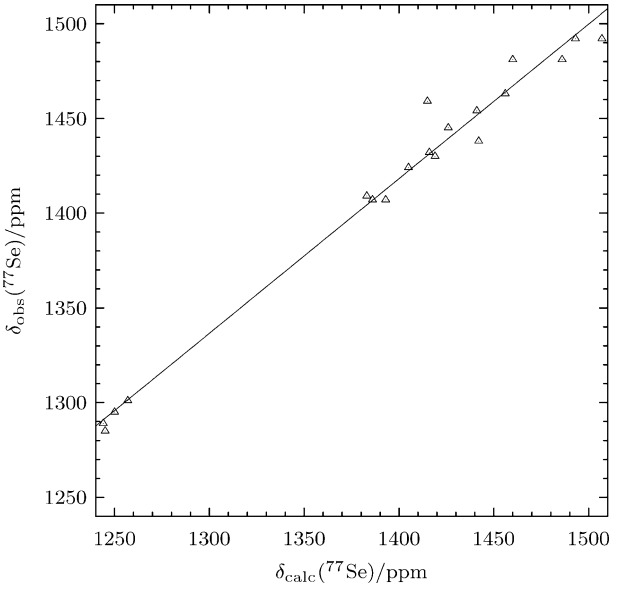


Figure 14. Linear correlation between calculated [δ_{calc}, PBE1PBE/6-311++G(2d,p)] and observed (δ_{obs}) ^{77}Se NMR chemical shifts. Included are data of compounds **1**–**14** (both *syn*- and *anti*-isomer if existent). The correlation is described by the linear equation $\delta_{obs}(^{77}Se)/ppm = 0.83(3) \cdot \delta_{calc}(^{77}Se)/ppm + 2.6(4) \times 10^2$.

$$\delta_{obs}(^{13}C)/ppm = 0.984(7) \cdot \delta_{calc}(^{13}C)/ppm - 2.4(5)$$

This clearly allows NMR signal assignment based on calculated values. The correlation for ^{77}Se NMR shifts (see the following equation and Figure 14) is less accurate.

$$\delta_{obs}(^{77}Se)/ppm = 0.83(3) \cdot \delta_{calc}(^{77}Se)/ppm + 2.6(4) \times 10^2$$

 © 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

NBO Analyses

The bonding situation in the described compounds was analysed by means of natural bond orbital (NBO) theory.[26] The results are very similar for all compounds with 1,2- and 1,3-diols, respectively. Therefore the results obtained for **1** and **8** which are discussed in the following are representative for all compounds.

In the five-membered ring of **1** as well as in the six-membered ring of **8** the selenium atom bears a positive natural charge of +1.9. The exocyclic oxygen atoms bear a natural charge of –1.0 and the endocyclic ones a charge of –0.8. In agreement with the calculated and observed endocyclic O–Se–O angles, the selenium contribution (natural hybrid orbital, NHO) to the Se–O single bonds in **1** has a slightly higher p character than in the case of **8**. In all cases, d orbital contributions are negligible. Numerical values are provided in Table 2.

Figure 15 shows isocontour plots of selected natural bond orbitals of **8**. Subfigures b and d show the valence-shell lone pair at the selenium atom. The predominant s character (about 70%, Table 2) is apparent. Together with the high positive natural charge on Se the intermolecular contacts described above can be understood as Lewis acid-base interactions where Se^{IV} is the Lewis acid.

Subfigure 15g illustrates the overlap between a p type lone pair at the exocyclic oxygen atom and one of the two endocyclic σ*(Se–O) orbitals. A second-order-perturbation-theory analysis performed with the NBO program package shows that this overlap gives rise to a two-electron stabilisation energy of 51 kJ mol^{-1}. Actually, the interactions between the second p type lone pair (not shown in the Figure) and the σ*(Se–O) orbitals lead to stabilisation energies of 76 kJ mol^{-1}. Therefore the exocyclic Se–O bonds in dialkyl-selenites can be described by a σ bond and a set of four negative hyperconjugations between filled n_π orbitals (two p type lone pairs) and the adjacent σ*(Se–O) orbitals. From the results of the NBO analysis it is clear that the Lewis structure in Figure 16 (a) does not give an appropriate description of the real bonding situation in dialkyl selenites. The alternative dipolar structure (Figure 16, b) does not take into account that the bond orders of endocyclic and exocyclic Se–O bonds differ by a factor of about two. For a correct description of both charges and bond orders a resonance (Figure 16, e) between the formulae in Figure 16 (a–d) may be considered.

Table 2. Selected results of DFT calculations and NBO analyses for compounds **1** and **8**.

		1		**8**	
bond lengths [Å]	Se=O	1.611		1.620	
	Se–O	1.813	1.808	1.795	1.795
bond angles [°]	O–Se=O	104.5	108.4	105.4	105.5
	O–Se–O	88.9		95.3	
NBO charges	Se	+1.91		+1.93	
	=O	–0.96		–0.99	
	–O	–0.79	–0.79	–0.79	–0.79
NHO at Se	Se=O	$sp^{5.66}$		$sp^{5.91}$	
	Se–O	$sp^{12.79}$	$sp^{13.42}$	$sp^{11.55}$	$sp^{11.55}$
	LP	$sp^{0.37}$		$sp^{0.41}$	

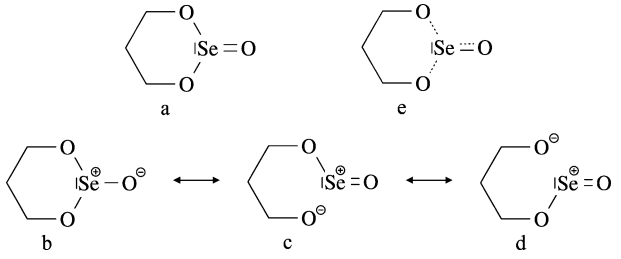


Figure 16. Resonance structures for **8**.

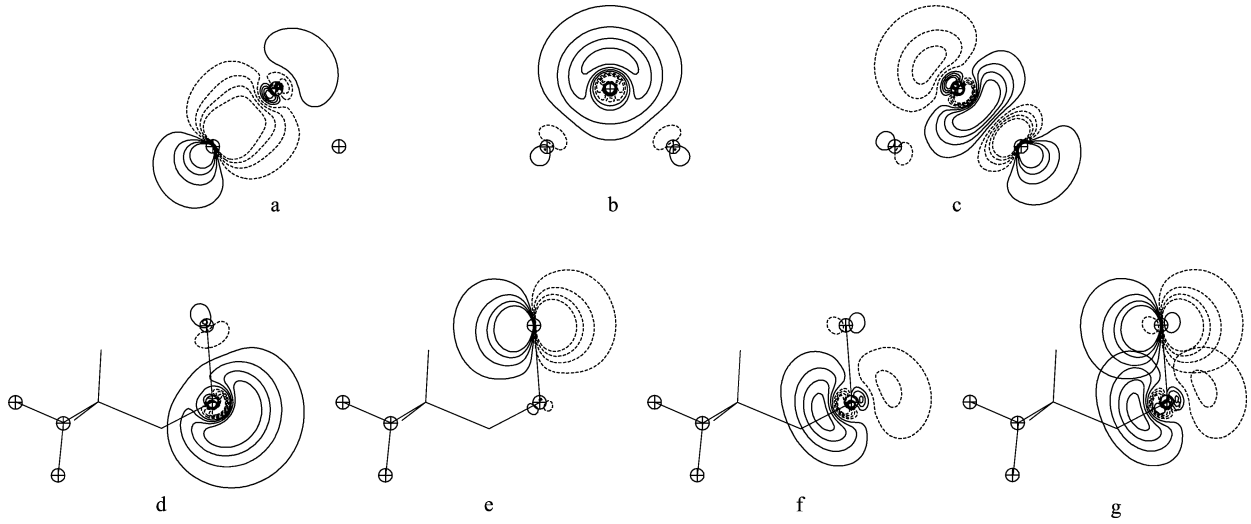


Figure 15. Isocontour plots of selected natural bond orbitals in **8**. Isolines are drawn at 0.03, 0.08, 0.13 and 0.18. Crossed circles indicate atoms in the drawing plane. (a) Se–O bonding σ orbital, (b) lone pair on Se, (c) Se–O antibonding σ* orbital, (d) lone pair on Se, (e) lone pair on terminal oxygen atom, (f) Se–O antibonding σ* orbital, (g) negative hyperconjugation between (e) and (f).

 © 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Conclusions

Well-defined carbohydrate derivatives of selenium(IV) form in agreement with the stereochemical properties of the carbohydrate's selenium-binding site. It was shown that this binding site can be determined unambiguously by means of the coordination-induced shift (CIS) of NMR signals. The basis of an unusually reliable structure–CIS correlation is a perfect match between experimentally observed and theoretically derived chemical shift values.

The analyses of the bonding situation showed that there are, as is usual in p-block chemistry, no significant contributions of selenium d orbitals. The shape and extension of the valence-shell lone pair of selenium in the alkylene selenites are dominated by an s character of about 70%. Accordingly, the endocyclic O–Se bonds are mostly of p character which results in endocyclic O–Se–O angles of about 90°. The oxyselenium(IV) core thus provides a binding site that matches the relatively small bite of an alkylenedioxy substituent. This substituent, in coordination chemistry addressed as a diolato ligand, provides unstrained chelate rings either for small tetrahedral centres such as carbon or boron or for centres that demand bonding at about right angles: octahedral centres, axial-equatorial pairs of trigonal bipyramids, or, in this work, a low-coordinate centre the bonding directions of which are p orbital dominated.

Taking together the predominant s character of the selenium's lone pair and a natural charge of about +2, the selenium centre is a typical Lewis acid which has been recognised from the crystal structure's packing principles of the pinacol derivative.[24]

Keeping in mind the issue of the hydrolytic sensitivity of a p-block centre–biomolecule chelate, the most significant property of the selenites reported herein is that rapid hydrolysis is restricted to pH values larger than the acidity constant of selenious acid. Moreover, an aqueous solution of unprotolysed $(HO)_2SeO$ is a suitable starting material for the formation of diol esters, that is, for the replacement of two hydroxy groups by a single alkylenedioxy substituent in favour of the chelate effect. The hydrolytic equilibrium thus appears to be correlated with and controllable by the acid's protonation state.

Supporting Information (see also the footnote on the first page of this article): Additional figures (intermolecular contacts in **3**, **9**, **10** and **11**. ^{77}Se NMR spectrum of **16**) and tables (NBO analyses).

Experimental Section

Quantum Chemical Calculations: Performed with GAUSSIAN 03[28] and NBO 5.0.[26]

Materials: Reagent-grade chemicals were purchased from Fluka, Sigma Aldrich and Acros and used as supplied. Methyl β-D-ribopyranoside was obtained from Glycon Biochemicals. 1,1′-Bicyclohexyl-1,1′-diol,[29] 1,1-bis(hydroxymethyl)cyclopentane[30] and methyl β-D-ribofuranoside[31] were prepared according to literature procedures.

NMR Spectra: All measurements were performed at room temperature. Spectrometers: Jeol Eclipse 270 (^{1}H: 270 MHz, ^{13}C: 67.9 MHz, ^{77}Se: 51.5 MHz) and Jeol Eclipse 400 (^{1}H: 400 MHz, ^{13}C: 101 MHz, ^{77}Se: 76.2 MHz) NMR spectrometers. The signals of the deuterated solvent (^{13}C) and the residual protons therein (^{1}H) were used as an internal secondary reference for the chemical shift. ^{77}Se shifts were referenced to external Me_2Se in $CFCl_3$. If necessary, ^{1}H and ^{13}C NMR signals were assigned by means of routine ^{1}H-^{1}H-COSY45, DEPT135, ^{1}H-^{13}C-HMQC and ^{1}H-^{13}C-HMBC experiments. Ratios of isomers were determined from suitable ^{1}H integrals where possible. The abbreviations "a" (*anti*) and "s" (*syn*) are used in the assignment of NMR signals.

Infrared Spectra: Jasco FTIR 460 Plus spectrometer equipped with a PIKE MIRacle ATR unit.

Crystal Structure Determination and Refinement: Crystals suitable for X-ray crystallography were selected with the aid of a polarising microscope, mounted on the tip of a glass fibre and investigated at 200(2) K on a Nonius KappaCCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by Patterson methods (SHELXS-97[32]) and refined by full-matrix, least-squares calculations on F^2 (SHELXL-97[32]). Hydrogen atoms were included in idealised positions with one common isotropic displacement parameter refined. Anisotropic displacement parameters were refined for all non-hydrogen atoms. Multi-scan absorption corrections were performed with SCALEPACK[33] or SADABS.[34] Crystallographic data are listed in Tables 3 and 4. Publication material was prepared with PLATON[35] and ORTEP-III[36].

CCDC-647110 (for **3**), -647111 (for **6**), -647112 (for **7**), -647113 (for **9**), -647114 (for **10**), -647115 (for **11**), -647116 (for **12**), -647117 (for **13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Procedure for Selenite Synthesis: A stirred suspension of equimolar amounts of selenium dioxide and the diol in cyclohexane or dioxane (40 mL) was heated to reflux at a water trap for 1–8 h. The solvent was distilled and the crude product was freed from traces of solvent under reduced pressure. Unless otherwise stated, this method afforded products of analytical purity. Crystals for X-ray structure analyses were grown by recrystallisation from cyclohexane or chloroform.

(EthdH$_{-2}$)SeO (1): Prepared from ethane-1,2-diol (1.24 g, 20.0 mmol) and selenium dioxide (2.22 g, 20.0 mmol) in cyclohexane according to the general procedure. Pure **1** (2.94 g, 19.0 mmol, 95%) was immediately obtained as a colourless powder. M.p. 65–67 °C. ^{77}Se NMR (51.5 MHz, $CDCl_3$, 26 °C): δ = 1430 ppm. ^{1}H NMR (270 MHz, $CDCl_3$, 24 °C): δ = 4.72–4.30 (m, characteristic AA′BB′ pattern) ppm. ^{13}C NMR (67.9 MHz, $CDCl_3$, 26 °C): δ = 70.5 ppm. IR: $\tilde{\nu}$ = 2956, 2897, 1447, 1331, 1206, 1017, 917, 882 cm^{-1}. MS (DCI$^+$, isobutane) *m*/*z* calcd. for $C_2H_5O_3Se$ [M + H]$^+$ 156.9; found: 157.0 with a characteristic Se_1 pattern. $C_2H_4O_3Se$ (155.01): calcd. C 15.50, H 2.60; found C 15.71, H 2.60.

(*rac*-1,2-PrpdH$_{-2}$)SeO (2): Prepared from *rac*-propane-1,2-diol (1.52 g, 20.0 mmol) and selenium dioxide (2.22 g, 20.0 mmol) in cyclohexane according to the general procedure. Pure **2** (3.16 g, 18.7 mmol, 93%), a mixture of four isomers, was immediately obtained as a colourless oil. ^{77}Se NMR (76.2 MHz, $CDCl_3$, 25 °C): δ = 1438 (*syn*), 1432 (*anti*) ppm. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 5.06–4.93 (m, 1 H_a; HC_{2a}), 4.72–4.63 (m, 1 H_a; HC_{1a}), 4.60–4.54 (m, 1 H_s; HC_{1s}), 4.53–4.45 (m, 1 H_s; HC_{2s}), 4.23–4.15 (m, 1 H_s; HC_{1s}), 3.88–3.75 (m, 1 H_a; HC_{1a}), 1.52–1.46 (m, 3 H_s; HC_{3s}), 1.40–1.36 (m, 3 H_a; HC_{3a}) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ

 © 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Table 3. Crystallographic data for **3**, **6**, **7** and **9**.

	3	**6**	**7**	**9**
CCDC number	647110	647111	647112	647113
Empirical formula	$C_5H_8O_3Se$	$C_{10}H_{16}O_3Se$	$C_{12}H_{20}O_3Se$	$C_5H_{10}OSe$
M_r [g mol^{-1}]	195.07	263.19	291.24	197.09
Crystal size [mm]	0.30 × 0.10 × 0.04	0.18 × 0.04 × 0.02	0.15 × 0.09 × 0.05	0.19 × 0.07 × 0.01
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	Cc
a [Å]	6.6558(2)	12.7738(4)	9.5109(3)	6.1588(5)
b [Å]	9.3066(3)	13.8258(5)	11.3210(3)	18.6338(12)
c [Å]	11.4501(4)	14.4208(6)	12.2766(3)	6.5158(4)
α [°]	94.1200(19)	112.8430(10)	82.8335(16)	90
β [°]	105.988(2)	101.086(2)	79.8575(17)	102.276(4)
γ [°]	98.352(2)	104.292(2)	74.1210(15)	90
V [Å^3]	669.91(4)	2152.83(15)	1247.45(6)	730.67(9)
Z	4	8	4	4
Calcd. density [g cm^{-3}]	1.9342(1)	1.6241(1)	1.5507(1)	1.7917(2)
μ [mm^{-1}]	5.535	3.468	3.001	5.075
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan
Transmission factor range	0.502–0.801	–	–	–
Reflections measured	20796	17522	10697	1569
R_{int}	0.0544	0.0384	0.0307	0.0230
Mean $\sigma(I)/I$	0.0359	0.0601	0.0430	0.0376
θ range	3.23–27.57	3.24–27.59	3.28–27.45	3.56–27.49
Observed reflections	2410	7165	4529	1391
x, y (weighting scheme)	0.0261, 0.3694	0.0587, 1.7359	0.0327, 0.4708	0.0403, 1.0458
Flack parameter	–	–	–	0.50(2) (inv. twin)
Reflections in refinement	3067	9835	5655	1561
Parameters	164	506	290	87
Restraints	0	0	0	2
$R(F_{obs})$	0.0281	0.0470	0.0319	0.0347
$R_w(F^2)$	0.0632	0.1231	0.0768	0.0828
S	1.033	1.006	1.034	1.084
Shift/error$_{max}$	0.001	0.001	0.001	0.001
Max. e$^-$ density [e Å^{-3}]	0.493	0.794	0.401	0.554
Min. e$^-$ density [e Å^{-3}]	–0.566	–0.696	–0.603	–0.501

= 80.9 (C_{2s}), 78.4 (C_{2a}), 75.9 (C_{1a}), 74.6 (C_{1s}), 17.4 (C_{3s}), 16.9 (C_{3a}) ppm. MS (DCI$^+$, isobutane) *m*/*z* calcd. for $C_3H_7O_3Se$ [M + H]$^+$ 171.0; found 171.0 with a characteristic Se_1 pattern. $C_3H_6O_3Se$ (169.04): calcd. C 21.32, H 3.58; found C 21.23, H 3.54.

(*cis*-1,2-CptdH$_{-2}$)SeO (3): Prepared from *cis*-cyclopentane-1,2-diol (3.07 g, 30.1 mmol) and selenium dioxide (3.34 g, 30.1 mmol) in cyclohexane according to the general procedure. Pure **3** (5.72 g, 29.3 mmol, 97%), a mixture of two isomers (*anti*/*syn* 3:1), was immediately obtained as a colourless crystalline solid. ^{77}Se NMR (51.5 MHz, $CDCl_3$, 26 °C): δ = 1481 (*syn*), 1463 (*anti*) ppm. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 5.43–5.38 (m; $HC_{1a,2a}$), 5.22–5.17 (m; $HC_{1s,2s}$), 2.32–1.60 (m) ppm. ^{13}C NMR (67.9 MHz, $CDCl_3$, 27 °C): δ = 91.2 ($C_{1s,2s}$), 88.1 ($C_{1a,2a}$), 33.7 ($C_{3s,5s}$), 32.8 ($C_{3a,5a}$), 22.1 (C_{4a}), 21.7 (C_{4s}) ppm. MS (DCI$^+$, isobutane) *m*/*z* calcd. for $C_5H_9O_3Se$ [M + H]$^+$ 197.0; found 197.1 with a characteristic Se_1 pattern. $C_5H_8O_3Se$ (195.08): calcd. C 30.78, H 4.13; found C 30.84, H 4.01.

(*cis*-1,2-ChxdH$_{-2}$)SeO (4): Prepared from *cis*-cyclohexane-1,2-diol (1.16 g, 10.0 mmol) and selenium dioxide (1.11 g, 10.0 mmol) in cyclohexane according to the general procedure. Pure **4** (1.98 g, 9.47 mmol, 95%), a mixture of two isomers, was immediately obtained as a colourless crystalline solid. ^{77}Se NMR (76.2 MHz, $CDCl_3$, 24 °C): δ = 1445 (*syn*), 1424 (*anti*) ppm. ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C): δ = 4.68–4.62 (m; $HC_{1a,2a}$), 4.40–4.34 (m; $HC_{1s,2s}$), 2.04–1.93 (m; $HC_{3s,6s}$), 1.82–1.69 (m; $HC_{3a,6a}$ and $HC_{3s,6s}$), 1.64–1.54 (m; $HC_{3a,6a}$), 1.54–1.47 (m; $HC_{4s,5s}$), 1.45–1.34 (m; $HC_{4a,5a}$), 1.24–1.11 (m; $HC_{4a,5a}$ and $HC_{4s,5s}$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 24 °C): δ = 81.0 ($C_{1s,2s}$), 79.7 ($C_{1a,2a}$), 28.8 ($C_{3s,6s}$), 28.1 ($C_{3a,6a}$), 20.8 ($C_{4s,5s}$), 20.5 ($C_{4a,5a}$) ppm. MS (DCI$^+$, isobutane) *m*/*z* calcd. for $C_6H_{11}O_3Se$ [M + H]$^+$ 211.0; found 211.1 with a characteristic Se_1 pattern. $C_6H_{10}O_3Se$ (209.10): calcd. C 34.46, H 4.82; found C 34.36, H 4.78.

(*rac-trans*-1,2-ChxdH$_{-2}$)SeO (5): Prepared from *rac-trans*-cyclohexane-1,2-diol (2.32 g, 20.0 mmol) and selenium dioxide (2.22 g, 20.0 mmol) in cyclohexane according to the general procedure. Pure **5** (3.97 g, 19.0 mmol, 95%) was immediately obtained as a colourless crystalline solid. M.p. 69.4–70.7 °C. ^{77}Se NMR (76.2 MHz, $CDCl_3$, 24 °C): δ = 1407 ppm. ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C): δ = 4.18–4.05 (m, 1 H), 3.67–3.54 (m, 1 H), 2.39–2.19 (m, 2 H), 1.95–1.79 (m, 2 H), 1.76–1.61 (m, 1 H), 1.59–1.46 (m, 1 H), 1.44–1.17 (m, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 87.1, 83.1, 30.7, 29.8, 23.9, 23.7 ppm. IR: $\tilde{\nu}$ = 2927, 2861, 1453, 1447, 1360, 1091, 1029, 1011, 932, 912, 882, 848, 837, 796, 653, 643 cm^{-1}. MS (DCI$^+$, isobutane) *m*/*z* calcd. for $C_6H_{11}O_3Se$ [M + H]$^+$ 211.0; found 211.2 with a characteristic Se_1 pattern. $C_6H_{10}O_3Se$ (209.10): calcd. C 34.46, H 4.82; found C 34.64, H 4.81.

(BptdH$_{-2}$)SeO (6): Prepared from 1,1′-bicyclopentyl-1,1′-diol (3.41 g, 20.0 mmol) and selenium dioxide (2.22 g, 20.0 mmol) in cyclohexane according to the general procedure. Pure **6** (5.10 g, 19.4 mmol, 97%) was immediately obtained as a colourless crystalline solid. M.p. 75.0–75.9 °C. ^{77}Se NMR (51.5 MHz, $CDCl_3$, 26 °C): δ = 1407 ppm. ^{1}H NMR (270 MHz, $CDCl_3$, 24 °C): δ = 2.33–2.15 (m, 2 H), 2.01–1.62 (m, 14 H) ppm. ^{13}C NMR

 © 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Table 4. Crystallographic data for **10**, **11**, **12** and **13**.

	10	**11**	**12**	**13**
CCDC number	647114	647115	647116	647117
Empirical formula	$C_5H_8O_3Se$	$C_7H_{12}O_3Se$	$C_4H_6O_4Se$	$C_6H_{10}O_6Se$
M_r [g mol^{-1}]	195.07	223.13	197.05	257.10
Crystal size [mm]	0.15 × 0.13 × 0.02	0.25 × 0.11 × 0.02	0.20 × 0.03 × 0.01	0.14 × 0.08 × 0.08
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_12_12_1$
a [Å]	4.72510(10)	21.1185(5)	4.37100(10)	6.0212(2)
b [Å]	24.3004(7)	6.5565(2)	11.7263(4)	10.8455(4)
c [Å]	5.9791(0)	12.7183(3)	11.4158(4)	13.1522(4)
α [°]	90	90	90	90
β [°]	111.3051(15)	107.3810(10)	100.781(2)	90
γ [°]	90	90	90	90
V [Å^3]	639.61(3)	1680.61(8)	574.80(3)	858.88(5)
Z	4	8	4	4
Calcd. density [g cm^{-3}]	2.0258(1)	1.7637(1)	2.2770(1)	1.9880(1)
μ [mm^{-1}]	5.797	4.425	6.465	4.369
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan
Transmission factor range	0.596–0.891	–	–	0.538–0.705
Reflections measured	10776	7610	2561	9216
R_{int}	0.0488	0.0418	0.0176	0.0344
Mean $\sigma(I)/I$	0.0323	0.0427	0.0244	0.0377
θ range	3.35–27.51	3.20–27.51	3.47–27.48	3.62–27.49
Observed reflections	1263	3222	1181	1815
x, y (weighting scheme)	0.0183, 0.8930	0.0707, 0.0685	0.0246, 0.3168	0.0109, 0.2880
Flack parameter	–	–	–	0.031(10)
Reflections in refinement	1456	3861	1317	1913
Parameters	83	201	80	132
Restraints	0	0	0	0
$R(F_{obs})$	0.0302	0.0422	0.0212	0.0231
$R_w(F^2)$	0.0638	0.1129	0.0532	0.0481
S	1.125	1.035	1.070	1.077
Shift/error$_{max}$	0.001	0.001	0.001	0.001
Max. e$^-$ density [e Å^{-3}]	0.467	0.640	0.440	0.373
Min. e$^-$ density [e Å^{-3}]	–0.729	–0.687	–0.476	–0.385

(67.9 MHz, $CDCl_3$, 26 °C): δ = 100.8 (C_1), 36.2/35.7 ($C_{2,5}$), 24.2/24.0 ($C_{3,4}$) ppm. IR: $\tilde{\nu}$ = 2953, 2871, 1448, 1430, 1173, 967, 938, 903, 866, 825, 656 cm^{-1}. MS (DCI$^+$, isobutane) *m/z* calcd. for $C_{10}H_{17}O_3Se$ [M + H]$^+$ 265.0; found 265.1 with a characteristic Se_1 pattern. $C_{10}H_{16}O_3Se$ (263.19): calcd. C 45.63, H 6.13; found C 45.92, H 6.11.

(BhxdH$_{-2}$)SeO (7): Prepared from 1,1′-bicyclohexyl-1,1′-diol (1.98 g, 10.0 mmol) and selenium dioxide (1.11 g, 10.0 mmol) in cyclohexane according to the general procedure. Pure **7** (2.68 g, 9.20 mmol, 92%) was immediately obtained as a colourless crystalline solid. M.p. 110.7–111.4 °C. ^{77}Se NMR (76.2 MHz, $CDCl_3$, 25 °C): δ = 1409 ppm. ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C): δ = 2.25–2.15 (m, 2 H), 1.84–1.63 (m, 12 H), 1.40–1.25 (m, 4 H), 1.22–1.07 (m, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 24 °C): δ = 92.6 (C_1), 32.4/32.2 ($C_{2,6}$), 25.4 (C_4), 22.1/21.9 ($C_{3,5}$) ppm. IR: $\tilde{\nu}$ = 2923, 2846, 1450, 1252, 1147, 1126, 937, 932, 918, 908, 898, 854, 834, 809, 732, 696, 646 cm^{-1}. MS (DCI$^+$, isobutane) *m/z* calcd. for $C_{12}H_{21}O_3Se$ [M + H]$^+$ 293.1; found 293.1 with a characteristic Se_1 pattern. $C_{12}H_{20}O_3Se$ (291.25): calcd. C 49.49, H 6.92; found C 49.50, H 7.03.

(1,3-PrpdH$_{-2}$)SeO (8): Prepared from propane-1,3-diol (1.52 g, 20.0 mmol) and selenium dioxide (2.22 g, 20.0 mmol) in cyclohexane according to the general procedure. Pure **8** (3.06 g, 18.1 mmol, 91%) was immediately obtained as a colourless powder. ^{77}Se NMR (51.5 MHz, $CDCl_3$, 26 °C): δ = 1301 ppm. ^{1}H NMR (270 MHz, $CDCl_3$, 24 °C): δ = 5.14–5.02 (m, 2 H, $HC_{1,3}$), 3.93–3.84 (m, 2 H, $HC_{1,3}$), 2.62–2.43 (m, 1 H, HC_2), 1.60–1.50 (m, 1 H, HC_2) ppm. ^{13}C NMR (67.9 MHz, $CDCl_3$, 26 °C): δ = 59.1 ($C_{1,3}$), 28.7 (C_2) ppm. MS (DCI$^+$, isobutane) *m/z* calcd. for $C_3H_7O_3Se$ [M + H]$^+$ 171.0; found 171.1 with a characteristic Se_1 pattern.

(DmpdH$_{-2}$)SeO (9): Prepared from 2,2-dimethylpropane-1,3-diol (2.08 g, 20.0 mmol) and selenium dioxide (2.22 g, 20.0 mmol) in cyclohexane according to the general procedure. Pure **9** (3.51 g, 17.8 mmol, 89%) was immediately obtained as a colourless crystalline solid. M.p. 86.4–87.1 °C. ^{77}Se NMR (76.2 MHz, $CDCl_3$, 25 °C): δ = 1285 ppm. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 4.72 (d, $^2J_{H,H}$ = 12 Hz, 2 H; $HC_{1,3}$), 3.38 (d, $^2J_{H,H}$ = 12 Hz, 2 H; $HC_{1,3}$), 1.28 (s, 3 H, H_3C), 0.78 (s, 3 H, H_3C) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 68.3 ($C_{1,3}$), 33.0 (C_2), 22.6/21.9 ($C_{4,5}$) ppm. IR: $\tilde{\nu}$ = 2977, 2965, 2876, 1474, 1457, 1396, 1371, 1362, 1310, 1033, 970, 899, 776 cm^{-1}. MS (DCI$^+$, isobutane) *m/z* calcd. for $C_5H_{11}O_3Se$ [M + H]$^+$ 199.0; found 199.1 with a characteristic Se_1 pattern. $C_5H_{10}O_3Se$ (197.09): calcd. C 30.47, H 5.11; found C 30.54, H 5.17.

(BhmrH$_{-2}$)SeO (10): Prepared from 1,1-bis(hydroxymethyl)cyclopropane (1.53 g, 15.0 mmol) and selenium dioxide (1.66 g, 15.0 mmol) in cyclohexane according to the general procedure. Pure **10** (2.82 g, 14.5 mmol, 96%) was immediately obtained as a colourless crystalline solid. M.p. 97–99 °C. ^{77}Se NMR (51.5 MHz, $CDCl_3$, 25 °C): δ = 1295 ppm. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 5.29 (d, $^2J_{H,H}$ = 12 Hz, 2 H; $HC_{1,3}$), 2.93 (d, $^2J_{H,H}$ = 12 Hz, 2 H; $HC_{1,3}$), 0.78–0.71 (m, 2 H, HC_4), 0.38–0.31 (m, 2 H, HC_5) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 66.5 ($C_{1,3}$), 19.8 (C_2), 12.2/7.6 ($C_{4,5}$) ppm. IR: $\tilde{\nu}$ = 3003, 2952, 2871, 1453, 1429,

 © 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

1381, 1330, 1049, 1028, 977, 947, 929, 911, 769 cm^{-1}. MS (DCI$^+$, isobutane) *m*/*z* calcd. for $C_5H_9O_3Se$ [M + H]$^+$ 197.0; found 197.1 with a characteristic Se_1 pattern. $C_5H_8O_3Se$ (195.08): calcd. C 30.78, H 4.13; found C 30.61, H 4.05.

(BhmtH$_{-2}$)SeO (11): Prepared from 1,1-bis(hydroxymethyl)cyclopentane (1.32 g, 10.1 mmol) and selenium dioxide (1.13 g, 10.1 mmol) in cyclohexane according to the general procedure. Pure **11** (2.07 g, 9.28 mmol, 92%) was immediately obtained as a colourless crystalline solid. M.p. 56.2–57.2 °C. ^{77}Se NMR (76.2 MHz, $CDCl_3$, 25 °C): δ = 1289 ppm. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 4.82 (d, ^2J(H,H) = 12 Hz, 2 H; $HC_{1,3}$), 3.45 (d, $^2J_{H,H}$ = 12 Hz, 2 H; $HC_{1,3}$), 1.98–1.93 (m, 2 H), 1.74–1.65 (m, 2 H), 1.65–1.56 (m, 2 H), 1.19–1.13 (m, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 67.0 ($C_{1,3}$), 44.7 (C_2), 33.25/33.22 ($C_{4,7}$), 25.2/24.5 ($C_{5,6}$) ppm. MS (DCI$^+$, isobutane) *m*/*z* calcd. for $C_7H_{13}O_3Se$ [M + H]$^+$ 225.0; found 225.1 with a characteristic Se_1 pattern. $C_7H_{12}O_3Se$ (223.13): calcd. C 37.68, H 5.42; found C 37.90, H 5.46.

(AnErytH$_{-2}$)SeO (12): Prepared from 1,4-anhydroerythritol (2.08 g, 20.0 mmol) and selenium dioxide (2.22 g, 20.0 mmol) in cyclohexane according to the general procedure. Pure **12** (3.71 g, 18.8 mmol, 94%), containing only *one* isomer, was immediately obtained as a colourless crystalline solid. M.p. 162.2–163.0 °C. ^{77}Se NMR (76.2 MHz, $CDCl_3$, 24 °C): δ = 1492 ppm. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 5.58–5.53 (m, 2 H, $HC_{2,3}$), 4.12–4.07 (m, 2 H, $HC_{1,4}$), 3.76–3.69 (m, 2 H, $HC_{1,4}$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 24 °C): δ = 87.2 ($C_{2,3}$), 73.7 ($C_{1,4}$) ppm. IR: $\tilde{\nu}$ = 2880, 1463, 1321, 1289, 1104, 1079, 1047, 1011, 982, 919, 854, 831, 814, 734, 650, 622, 607 cm^{-1}. MS (DCI$^+$, isobutane) *m*/*z* calcd. for $C_4H_7O_4Se$ [M + H]$^+$ 199.0; found 199.1 with a characteristic Se_1 pattern. $C_4H_6O_4Se$ (197.05): calcd. C 24.38, H 3.07; found C 24.19, H 2.92.

(Me-β-D-Rib*f*2,3H$_{-2}$)SeO (13): Prepared from methyl β-D-ribofuranoside (0.850 g, 5.18 mmol) and selenium dioxide (0.575 g, 5.18 mmol) in dioxane according to the general procedure. Pure **13** (1.15 g, 4.47 mmol, 86%), a mixture of two isomers, was immediately obtained as a colourless powder. ^{77}Se NMR (76.2 MHz, $CDCl_3$, 24 °C): δ = 1492 (syn), 1481 (*anti*) ppm. ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C): δ = 5.57 (ddd, $J_{H,H}$ = 5.8, $J_{H,H}$ = 1.4, $J_{H,H}$ = 0.6 Hz; HC_{3a}), 5.34 (ddd, $J_{H,H}$ = 6.3, $J_{H,H}$ = 1.7, $J_{H,H}$ = 0.6 Hz; HC_{3s}), 5.32–5.29 (m; HC_{2a} and HC_{1s}), 5.16 (ddd, $J_{H,H}$ = 6.3, $J_{H,H}$ = 1.1, $J_{H,H}$ = 0.6 Hz; HC_{2s}), 5.02 (s; HC_{1a}), 4.72–4.69 (m; HC_{4s}), 4.47–4.44 (m; HC_{4a}), 3.79–3.65 (m; HC_{5a} and HC_{5s}), 3.48 (s; HC_{6s}), 3.46 (s; HC_{6a}) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 24 °C): δ = 109.8 (C_{1s}), 109.3 (C_{1a}), 93.4 (C_{2s}), 91.0 (C_{2a}), 90.0 (C_{3s}), 88.3 (C_{4s}), 87.9 (C_{3a}), 87.7 (C_{4a}), 63.5 (C_{5a}), 63.4 (C_{5s}), 56.1 (C_{6s}), 55.9 (C_{6a}) ppm. IR: $\tilde{\nu}$ = 3384, 2941, 1191, 1098, 1068, 1035, 1010, 986, 925, 832, 807, 775, 678, 621 cm^{-1}. MS (DCI$^+$, isobutane) *m*/*z* calcd. for $C_6H_{11}O_6Se$ [M + H]$^+$ 259.0; found 259.0 with a characteristic Se_1 pattern. $C_6H_{10}O_6Se$ (257.10): calcd. C 28.03, H 3.92; found C 28.43, H 3.93.

(Me-β-D-Rib*p*3,4H$_{-2}$)SeO (14): Prepared from methyl β-D-ribopyranoside (0.821 g, 5.00 mmol) and selenium dioxide (0.555 g, 5.00 mmol) in dioxane according to the general procedure. Pure **14** (1.16 g, 4.51 mmol, 90%), a mixture of two isomers, was immediately obtained as a colourless powder. ^{77}Se NMR (76.2 MHz, [D$_6$]DMSO, 24 °C): δ = 1459 (*anti*), 1454 (*syn*) ppm. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 22 °C): δ = 5.71 (s, broad; HO), 5.49 (s, broad; HO), 4.91–4.87 (m; HC_{3a} and HC_{3s}), 4.74 (d, $J_{H,H}$ = 2.5 Hz; HC_{1s}), 4.60 (d, $J_{H,H}$ = 2.5 Hz; HC_{1a}), 4.46–4.41 (m; HC_{4a}), 4.19–4.15 (m; HC_{4s}), 3.87–3.83 (m; H_2C_{5a}), 3.77–3.72 (m; HC_{2s}), 3.69–3.63 (m; H_2C_{5s}), 3.58–3.53 (m; HC_{2a}), 3.32 (s; H_3C_{6s}), 3.29 (s; H_3C_{6a}) ppm. ^{13}C NMR (101 MHz, [D$_6$]DMSO, 24 °C): δ = 100.7 (C_{1a}), 98.9 (C_{1s}), 78.6 (C_{3s}), 77.4 (C_{3a}), 76.7 (C_{4s}), 75.3 (C_{4a}), 64.9 (C_{2a}), 63.6 (C_{2s}), 61.4 (C_{5s}), 58.4 (C_{5a}), 55.1 (C_{6s}), 54.8 (C_{6a}) ppm. IR: $\tilde{\nu}$ = 3475, 2918, 1733, 1419, 1355, 13251196, 1135, 1084, 1058, 1025, 998, 960, 917, 860, 835, 787, 741, 669, 619 cm^{-1}. MS (DCI$^+$, isobutane) *m*/*z* calcd. for $C_6H_{11}O_6Se$ [M + H]$^+$ 259.0; found 259.0 with a characteristic Se_1 pattern. $C_6H_{10}O_6Se$ (257.10): calcd. C 28.03, H 3.92; found C 28.06, H 3.81.

(Me-α-D-Man*p*2,3H$_{-2}$)SeO (15): Prepared from methyl α-D-mannopyranoside (1.94 g, 10.0 mmol) and selenium dioxide (1.11 g, 10.0 mmol) in dioxane according to the general procedure. Compound **15**, a mixture of two isomers, was obtained as a colourless powder. The solvent could not be removed completely. ^{77}Se NMR (76.2 MHz, [D$_6$]DMSO, 24 °C): δ = 1450 (*syn*), 1426 (*anti*) ppm. ^{13}C NMR (101 MHz, [D$_6$]DMSO, 24 °C): δ = 97.7 (C_{1s}), 97.4 (C_{1a}), 83.1 (C_{3a}), 82.5 (C_{3s}), 80.9 (C_{2s}), 77.9 (C_{2a}), 72.6 (C_{5s}), 71.8 (C_{5a}), 68.3 (C_{4a}), 68.1 (C_{4s}), 60.6 (C_{6s}), 60.2 (C_{6a}), 54.3 (C_{7a}), 54.1 (C_{7s}) ppm. MS (DCI$^+$, isobutane) *m*/*z* calcd. for $C_7H_{13}O_7Se$ [M + H]$^+$ 289.0; found 289.0 with a characteristic Se_1 pattern.

(Me-β-D-Xyl*p*2,3H$_{-2}$)SeO (16a) and (Me-β-D-Xyl*p*3,4H$_{-2}$)SeO (16b): Prepared from methyl β-D-xylopyranoside (1.64 g, 10.0 mmol) and selenium dioxide (1.11 g, 10.0 mmol) in dioxane according to the general procedure. A mixture of four isomers **16a** (*syn*/*anti*) and **16b** (*syn*/*anti*), was obtained as a colourless powder. The solvent could not be removed completely. ^{77}Se NMR (76.2 MHz, [D$_6$]DMSO, 24 °C): δ = 1447 (*syn*), 1446 (*syn*), 1432 (*anti*), 1431 (*anti*) ppm. ^{13}C NMR (101 MHz, [D$_6$]DMSO, 24 °C): δ = 105.5, 105.3, 103.1, 102.6, 86.7, 85.9, 83.8, 82.8, 81.0, 78.3, 77.9, 75.0, 73.5, 72.7, 69.9, 69.0, 66.8, 66.6, 63.5, 63.3, 56.8, 56.0, 55.8, 54.9 ppm. MS (DCI$^+$, isobutane) *m*/*z* calcd. for $C_7H_{13}O_7Se$ [M + H]$^+$ 259.0; found 259.0 with a characteristic Se_1 pattern.

Acknowledgments

The crystal structure of **12** was solved using a data set obtained on a crystal that had been prepared accidentally by Max Pfister and Richard Betz. We acknowledge their generous contribution.

[1] J. W. Wyeth, R. E. Pounder, A. E. Duggan, C. A. O'Morain, H. D. Schaufelberger, E. H. De Koster, E. A. J. Rauws, K. D. Bardhan, J. Gilvarry, M. J. M. Buckley, P. A. Gummett, R. P. H. Logan, *Aliment. Pharmacol. Ther.* **1996**, *10*, 623–630.
[2] K. Benner, P. Klüfers, *Carbohydr. Res.* **2000**, *327*, 287–292.
[3] P. Klüfers, O. Labisch, *Z. Anorg. Allg. Chem.* **2003**, *629*, 1441–1445.
[4] J. Burger, C. Gack, P. Klüfers, *Angew. Chem.* **1995**, *107*, 2950–2951; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2647–2649.
[5] R. Betz, P. Klüfers, unpublished results.
[6] K. Benner, P. Klüfers, J. Schuhmacher, *Z. Anorg. Allg. Chem.* **1999**, *625*, 541–543.
[7] K. Benner, P. Klüfers, M. Vogt, *Angew. Chem.* **2003**, *115*, 1088–1093; *Angew. Chem. Int. Ed.* **2003**, *42*, 1058–1062.
[8] P. Klüfers, F. Kopp, M. Vogt, *Chem. Eur. J.* **2004**, *10*, 4538–4545.
[9] X. Kästele, P. Klüfers, F. Kopp, J. Schuhmacher, M. Vogt, *Chem. Eur. J.* **2005**, *11*, 6326–6346.
[10] P. Klüfers, C. Vogler, *Z. Anorg. Allg. Chem.* **2007**, *633*, 908–912.
[11] P. Klüfers, P. Mayer, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1998**, *54*, 583–586.
[12] C. T. G. Knight, S. D. Kinrade, *A primer on the aqueous chemistry of silicon.* In *Studies in Plant Science*, vol. 8, 57–84; Elsevier Science B. V., **2001**.
[13] A. Michaelis, B. Landmann, *Justus Liebigs Ann. Chem.* **1887**, *241*, 150–160.
[14] F. Weygand, K. G. Kinkel, D. Tietjen, *Chem. Ber.* **1950**, *83*, 394–399.

 © 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

[15] H. P. Kaufmann, D. B. Spannuth, *Chem. Ber.* **1958**, *91*, 2127–2129.
[16] A. Simon, G. Heintz, *Naturwissenschaften* **1960**, 468.
[17] F. Dallacker, K.-W. Glombitza, M. Lipp, *Justus Liebigs Ann. Chem.* **1961**, *643*, 67–82.
[18] A. Simon, G. Heintz, *Chem. Ber.* **1962**, *95*, 2333–2343.
[19] C. A. Bunton, B. N. Hendy, *J. Chem. Soc.* **1963**, 3137–3140.
[20] K. Ballschmiter, H. Singer, *Chem. Ber.* **1968**, *101*, 7–16.
[21] H. Provendier, C. Santini, J.-M. Basset, L. Carmona, *Eur. J. Inorg. Chem.* **2003**, 2139–2144.
[22] A. Simon, R. Paetzold, *Z. Anorg. Allg. Chem.* **1960**, *303*, 53–71.
[23] D. B. Denney, D. Z. Denney, P. J. Hammond, Y. F. Hsu, *J. Am. Chem. Soc.* **1981**, *103*, 2340–2347.
[24] D. Dakternieks, R. W. Gable, B. F. Hoskins, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1989**, *45*, 206–208.
[25] D. R. Lide (Ed.), *CRC Handbook of Chemistry and Physics*, Taylor & Francis CRC Press, 87. edition, **2006**.
[26] E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, F. Weinhold, *NBO 5.G*, Theoretical Chemistry Institute, University of Wisconsin, Madison, **2001**.
[27] D. Cremer, J. A. Pople, *J. Am. Chem. Soc.* **1975**, *97*, 1354–1358.
[28] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03, Revision B.03 and D.01.*, Gaussian, Inc., Wallingford CT, **2004**.
[29] E. J. Corey, R. L. Danheiser, S. Chandrasekaran, *J. Org. Chem.* **1976**, *41*, 260–265.
[30] D. Domin, D. Benito-Garagorri, K. Mereiter, J. Frohlich, K. Kirchner, *Organometallics* **2005**, *24*, 3957–3965.
[31] R. Barker, H. G. Fletcher, *J. Org. Chem.* **1961**, *26*, 4605–4609.
[32] G. M. Sheldrick, *SHELX-97*, Release 97-2, **1997**.
[33] Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307–326.
[34] G. M. Sheldrick, *SADABS, Multi-Scan Absorption Correction Program*, version 2, **2001**.
[35] A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, **1980–2007**.
[36] L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.

Received: August 9, 2007
Published Online: November 8, 2007

 © 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim