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Caged Chalcogens: Theoretical Studies on a Tetracoordinated Oxonium Dication and Its Higher Homologues

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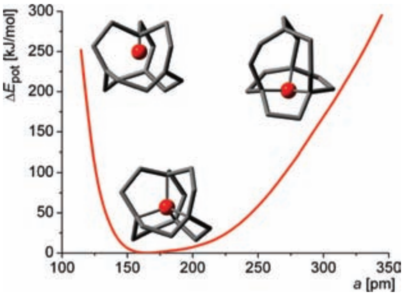
ABSTRACT



Tetravalent chalcogenium ions utilizing a hydrocarbon cage have been investigated by theoretical means with respect to their geometries and their electronic structure using DFT as well as MP2 calculations. In all cases—even for oxygen—we predict thermodynamically stable molecular entities with chalcogens coordinated by four carbon atoms.

Protonated water was first postulated more than 100 years ago[1] and had a major impact on the development of the acid−base theory of Brønsted and Lowry.[2] In fact, H_3O^+ ions have been isolated and well characterized by several techniques including vibrational[3] and NMR spectroscopy[4] as well as neutron[5] and X-ray diffraction.[6] The organic counterparts of H_3O^+ ions, the oxonium ions (R_3O^+), are widely known as intermediates of various transformations in organic chemistry. Furthermore, isolable congeners (commonly with non-nucleophilic counterions, e.g., BF_4^-, PF_6^-, or SbF_6^-) such as the Meerwein salt Me_3OBF_4 (**1**)[7] serve as highly powerful alkylation reagents and should be handled with extreme care. Since Meerwein's work in the 1950s, many reports on oxonium ions have been presented.[8] However, only a few examples exist where the trivalent oxygen is located within an oligocyclic framework.[9−12] The first bicyclic example **2** was described in 1965.[9] Recently, Olah reported the synthesis of an analogous oxaadamantane **3**.[12] Whereas the two latter examples are also highly reactive compounds that immediately undergo ring-opening reactions in the presence of

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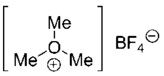
water or other nucleophiles, Mascal presented a series of tamed oxonium ions **4−6** that lost their typical reactivity toward nucleophiles.[13] Most surprisingly, NMR spectra of cation **4** could even be recorded in water.



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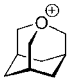

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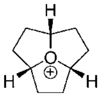

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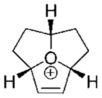

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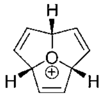

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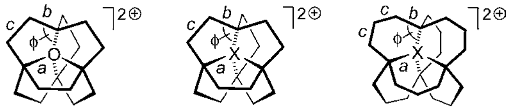
From the very early days on, theoretical chemistry has been a powerful tool to investigate strained molecular entities with unusual types of bonding.[14]

An obvious, however striking, idea is to utilize the remaining lone pair at the cationic oxygen of the trivalent oxonium ions for further binding to a proton or carbocation.[15,16] This idea inspired the design of the hexacyclic dication **7** with a caged oxygen atom (Figure 1). In other words, this molecular entity can also be seen as an oxide anion that is coordinated by a tetradentate tetracation.



7

8 (X = S)
9 (X = Se)
10 (X = Te)

11 (X = O)
12 (X = S)
13 (X = Se)
14 (X = Te)

Figure 1. Caged oxygen dication **7**, higher homologues **8−10**, enlarged cage compounds **11−14**, and definition of the most relevant geometrical parameters (used in Table 1).

As part of our ongoing studies with respect to methods for the annelation and spiroannelation of THF moieties,[17] we elucidate in this communication the possibility to involve the remaining lone pair in bonding. For better comparison of such species revealing unusual coordination modes, we investigated also cage compounds **8−10** with the heavier homologues of oxygen, namely, sulfur, selenium, and tellurium, as guests of the cage.[18,19] Furthermore, we also varied the size of the cage. Instead of a system consisting of five-membered rings, an analogous cage was computed on the basis of six-membered rings, or to put it in this way, we used propano bridges to tether the four carbocation centers. This approach led to the design of cage compounds **11−14** (Figure 1).[20]

For all compounds **7−14** the geometrical parameters were optimized (without any symmetry restrictions) using density functional theory (DFT)[21] by applying the three-parameter hybrid functional by Becke (B3)[22] and the correlation functional by Lee, Yang, and Parr (LYP).[23] As the basis set we used 6-311G(d) as suggested by Pople et al.,[24,25] implemented in Gaussian 03.[26] All minima were characterized by harmonic vibrational frequency calculations (NImag = 0), and all energies are corrected by zero-point vibrational energies.

In Table 1, we list the most important geometrical parameters including bond lengths *a*, *b*, and *c* as well as bond angles φ for **7−14**. In Figure 2, we have depicted as examples the optimized structures of the oxonium dication **7** and the telluronium dication **10**, using in both cases the smaller hydrocarbon cage. For the smaller cage compounds **7−10**, we observe in all cases tetravalent chalcogens revealing the typical tetrahedral angle of about 109° at the chalcogen. A comparison of the four distances *a* between the caged heteroelement and the four carbon centers reveals that these distances are almost the same. As anticipated, with increasing size of the chalcogen, this

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Table 1. Most Important Geometrical Parameters *a*, *b*, *c*, and φ (as Defined in Figure 1) of **7**−**14** (Calculated at the B3LYP/6-311G(d) Level of Theory), Wiberg Bond Indices (WBI),[27] Complexation Energies, Natural (NPA) Charges, and Chemical Shifts δ (Calculated at the B3LYP/6-311++G(2df, 2pd) Level of Theory)

	7	**8**	**9**	**10**	**11**[f]	**12**	**13**	**14**
a[a] [pm]	165.4[h]	175.4[h]	184.4[h]	195.8[h]	150.3/267.9[f]	199.4	209.8	217.2
b[a] [pm]	152.4	158.0	159.4	161.7	154.7/147.9[f]	154.0	154.0	155.1
c[a] [pm]	154.3	157.6	160.0	163.6	154.0[g]	153.7	154.8	154.3
φ[a] [deg]	99.9	99.1	97.5	95.4	110.0/95.7	106.4	105.4	105.3
WBI (X-C)[b]	0.55	0.94	0.93	0.86	0.81/0.10[f]	0.82	0.82	0.84
NPA Charge (X)[b] [e]	−0.515	+1.412	+1.814	+2.736	−0.646	+0.998	+1.201	+1.935
NPA Charge (C)[b] [e]	+0.409	−0.151	−0.233	−0.437	+0.331/+0.519	−0.001	−0.033	−0.211
ΔH_f [kJ/mol][c]	5143	3845	3677	3360	4600	3632	3647	3559
δ (C) [ppm] [d]	168.6	86.7	76.2	–[e]	94.4/330.6[f]	120.0	122.2	–[e]
δ ($\underline{C}H_2$) [ppm][d]	45.0	51.5	53.2	–[e]	42.9[g]	41.6	42.7	–[e]
δ ($C\underline{H}_2$) [ppm][d]	3.18	3.31	3.23	–[e]	2.82[g]	2.38	2.40	–[e]
δ ($\underline{X}$) [ppm][i,j]	452.4	214.6	1462	–[e]	91.4	−270.3	192.8	–[e]

[a] Mean value of all the corresponding values. [b] Calculated by a natural bond orbital (NBO) analysis using the B3LYP/6-311G(d) density. [c] The values of ΔH_f are based on the energies of a tetracation and a chalogenide dianion and are not corrected for basis set superposition effects (BSSE). [d] Relative to tetramethylsilane. [e] Due to problems to achieve reliable chemical shifts using basis sets for Te, we abstained from calculating them. [f] A tetrahydropyrane derivative with two distinct carbocationic centers is observed; two mean values are given. [g] Mean value due to problems with the assignment. [h] For comparison: the corresponding distances for trivalent chalogenium ions were calculated (see Supporting Information): 152.8 pm (O), 187.3 pm (S), 201.4 pm (Se), 217.2 pm (Te). [i] Relative to H_2O, SO_4^{2-}, and Me_2Se, respectively. [j] For quadrupolar ^{17}O and ^{33}S, such signals should be experimentally detectable, owing to the vanishing (or very small) electric field gradient at tetrahedral symmetry.

mean value steadily increases (Table 1). The larger size of selenium and tellurium is also mirrored in the increase of distance *b* and illustrates the strain associated with the hosting of these heavier elements (up to 162 pm in **10**).

Another parameter that describes the strain of the cage is the angle φ: values higher than 90° show an attractive interaction between the chalcogen and the former trivalent carbon. Whereas in the larger cage series **11**−**14** much higher values of φ are observed indicating enough space for the heavier chalcogens, the smaller cage compounds **7**−**10** show angles between 95° and 100°. The cage of compound **11** is much too large to force contacts between the oxygen and all cationic centers. Instead of tetra- or tricoordinated oxygen, a tetrahydropyrane structure with divalent oxygen and two discrete carbocations is observed. Therefore, Table 1 shows two highly different values for the respective bond lengths and angles.

A natural bond orbital analysis reveals that the Wiberg bond indices (WBI)[27] are only 0.55 for the oxygen containing congener **7**, whereas for **8**−**10** the corresponding bond indices are in the range between 0.86 and 0.94. Due to the smaller cage in **8**−**10**, these values are even larger than for the respective tetravalent species **12**−**14** using the greater cage (WBIs of 0.81−0.84). The natural population analysis afforded also natural charges presented in Table 1 for the heteroelement (X) and the carbocationic centers (C). As the only chalcogen of the series, oxygen carries a negative charge in **7** as well as in **11**. As expected, with increasing size and decreasing electronegativity of the chalcogen, the guest is able to accommodate more positive charge.

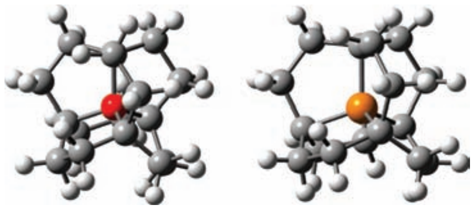

Figure 2. Optimized structures of the dications **7** (left) and **10** (right) as calculated on the level of B3LYP/6-311G(d).

As already mentioned, these dications can also be seen as chalcogenide anions complexed by a tetradentate tetracation. To get an impression of the energy associated with such a conceivable complexation process, we calculated also the potential energies of the separated ions on one side and the potential energy of the corresponding dications on the other (see Supporting Information). Their difference can be considered as complexation energy and is denoted as ΔH_f in Table 1. For the smaller cage compounds **7**−**10**, the ΔH_f value decreases with increasing size of the heteroelement. This behavior reflects the decreasing ionic character of the X−C bonds (X = O, S, Se, Te) when going from **7** to **10** as well as the limited space of the cage.

To test the flexibility of the chalcogen guest in the cage, we performed relaxed energy scans of the dications **7**−**10** by varying one of the distances *a*. These results are illustrated in Figure 3. It is noteworthy that the potential energy surface of compound **7** is relatively flat revealing a high flexibility of the caged oxygen, whereas for the other three congeners the geometry of the cage is rather

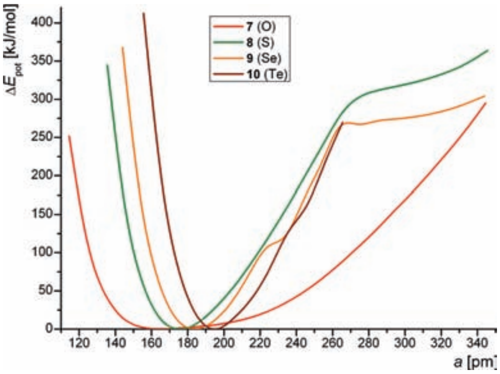

Figure 3. Potential energy of the dications **7−10** depending on the distance *a* between the caged chalcogen and one carbocationic center according to B3LYP/6-311G(d).

stable. The bending of the curves in the case of **8** and **9** at distances of about 260−270 pm mirrors the fact that at higher distances the trivalent chalcogenium ions play the crucial role. Between 260 and 330 pm, the chalcogen (S, Se) moves through a plane of three carbocationic centers. This movement is only associated with subtle changes of the potential energy. For **10** scanning the distance *a* further than 260 pm led to the destruction of the dication because the tellurium center bursts its host when moving out of the cage.

For the optimized oxygen-, sulfur-, and selenium-caged dications **7−9** and **11−13**, we also calculated the NMR chemical shifts (δ) of the most relevant carbon, hydrogen, and chalcogen atoms (Table 1). Whereas the ^{1}H NMR chemical shifts do not reveal any significant differences within the series, the ^{13}C NMR shifts demonstrate again the special case of the oxygen-caged compound **7**. For the carbocationic centers, a characteristic shift of 169 ppm was computed. This value is much more downfield-shifted than for the sulfur- and selenium-caged congeners **8** and **9** (87 and 76 ppm, respectively) but much more upfield-shifted than for discrete carbocations as in **11** (268 ppm).[28]

To take electron correlation effects into account that often play a crucial role in weak interactions,[29] we investigated the dications **7−10** also by means of the MP2[30] levels of theory (MP2/6-311G(d)). The most important geometrical parameters, WBIs and natural charges, are given in Table 2. With the exception of the tellurium-containing congener **10**, the distances between the central chalcogen and the carbocationic centers are even shorter than the corresponding ones obtained by B3LYP.

Table 2. Most Important Geometrical Parameters of **7−10** (Calculated at the MP2/6-311G(d) Level of Theory), Wiberg Bond Indices (WBI),[27] and Natural (NPA) Charges

	7	**8**	**9**	**10**
a^{a} [pm]	162.4	173.6	182.5	195.8
b^{a} [pm]	151.8	157.1	158.6	161.6
c^{a} [pm]	153.7	156.9	158.9	163.9
φ^{a} [deg]	100.2	98.9	97.1	95.6
WBI (X-C)^{b}	0.52	0.95	0.95	0.86
NPA Charge (X)^{b} [e]	−0.657	+1.433	+1.897	+2.732
NPA Charge (C)^{b} [e]	+0.482	−0.159	−0.259	−0.434

^{a} Mean value of all the corresponding values. ^{b} Calculated by a natural bond orbital (NBO) analysis using the MP2/6-311G(d) density.

Of course, computational studies of cations should always include realistic anions.[31] Therefore, we repeated the DFT calculations with two PF_6^- as counterions (see Supporting Information). The geometrical parameters of the tetravalent sulfur, selenium, and tellurium cage compounds **8−10** differ only slightly from the respective values given in Table 1. However, the oxygen-containing compound **7** is strongly distorted, as anticipated by the flat potential depicted in Figure 2. Therefore, we computed in the latter case also rather large noncoordinating anions[32] such as tetraphenylborates. Using these species as counterions, the tetracoordination of oxygen in **7** with almost equal bond lengths stays intact.

In conclusion, our investigations by means of B3LYP and MP2 level of theory demonstrate that tetravalent chalcogenium ions are local minima on their potential energy surface. Even for tetravalent oxygen, these highly remarkable dicationic species should be accessible when appropriate cages and large noncoordinating anions are provided. Our calculations may guide synthetic organic chemists to create these fascinating target molecules.

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Supporting Information Available: Gaussian Archive Entries and optimized structures for all calculated species. Full ref 26. This material is available free of charge via the Internet at http://pubs.acs.org.

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