CHEMISTRY
A European Journal

A Journal of
ChemPubSoc Europe

Accepted Article

Title: Anion recognition by neutral chalcogen bonding receptors: experimental and theoretical investigation

Authors: Encarnación Navarro-García, Bartomeu Galmés, María D Velasco, Antonio Caballero, and Antonio Frontera

To be cited as: *Chem. Eur. J.* 10.1002/chem.201905786

Link to VoR: http://dx.doi.org/10.1002/chem.201905786

Supported by
ACES

WILEY-VCH

10.1002/chem.201905786

WILEY-VCH

FULL PAPER

Anion recognition by neutral chalcogen bonding receptors: experimental and theoretical investigation

Encarnación Navarro-García,[a] Bartomeu Galmés,[b] María D. Velasco,[a] Antonio Frontera[b]* and Antonio Caballero[a]*

Dedication ((optional))

Abstract: The utilization of neutral receptors for the molecular recognition of anions based on chalcogen bonding (ChB) is an undeveloped area of host–guest chemistry. In this manuscript, the synthesis of two new families of sulfur, selenium and tellurium-based ChB binding motifs are reported. The stability of the thiophene, selenophene and tellurophene binding motifs has enabled the determination of association constants for ChB halide anion binding in the polar aprotic solvent THF by ^{1}H-, ^{77}Se- and ^{125}Te-NMR experiments. We have used two different aromatic cores and incorporated one or two Ch-binding motifs with the purpose to encapsulate the anion offering up to two concurrent chalcogen bonds. Theoretical calculations and NMR experiments reveal that, for S and Se receptors, hydrogen bonding interactions involving the acidic H-atom adjacent to the chalcogen atom are energetically favored over the ChB interaction. However, for the tellurophene binding motif, the σ-hole interaction is competitive and more favored than the H-bond.

Introduction

The hydrogen bond is undoubtedly the most important and prevalent noncovalent interaction.[1-7] However, other elements belonging to groups 14 to 17 of the periodic table have a similar function.[8–13] The electron density distribution in covalently bonded heavy atoms of groups 15 to 17 is anisotropic and frequently presents regions of positive (σ-holes) and negative (σ-lumps) electron density.[14–15] The location of the σ-hole is opposite to the covalent bond and the number of σ-holes usually coincides with the number covalent bonds formed by the main group element.[16]

Chalcogen bonding (ChB) is a subgroup of the σ-hole family that originates from the interaction between an electron rich atom or group of atoms and the σ-hole of an element belonging to group 16.[17-20] In fact, chalcogen bonding has been recently defined by a IUPAC commission as “net attractive interaction between an electrophilic region associated with a chalcogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity”.[21] The ChB interaction is more directional than hydrogen bonding (HB) and comparable to her sister halogen bonding (XB), however the presence of two σ-holes (opposite to both covalent bonds) confers to this interaction more possibilities of binding and fine tuning of the σ-holes individually. Compared to HB, both ChB and XB interactions have greater hydrophobicity and they are less sensitive to solvent effects and pH.[22,23] The binding strength of ChB is comparable to the ubiquitous HB and its high directionality allows greater precision in three dimensional spatial control. In fact, these distinctive characteristics of ChBs have been used in crystal engineering,[24,25] pharmaceutics,[26] catalysis,[27-29] anion transport,[30] self-assembly processes[31] and materials design.[32] However, studies of ChB interactions in solution remain scarce.[33,20] For instance, Zibarev *et al*.[34] have reported the association constants of dicyanotelluradiazole and dicyanoselenadiazole with anions measured using optical absorbance spectroscopy. Moreover, a systematic study in solution of the ability of several benzotelluradiazole derivatives as anionic receptor has been also reported.[35] Finally, Bryce’s group has used benzylic selenocyanates for anion binding in the solid state and solution, as evidenced by ^{13}C and ^{77}Se NMR spectroscopy.[36]

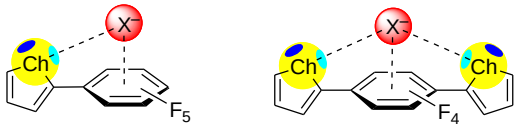
In the solid state, several motifs have been used for the design of supramolecular assemblies based on ChB interactions, including benzoselenazoles/tellurazoles,[37] tellurazole N-oxides,[30] bis-thiophenes/tellurophene,[38] etc.[39,40] However, the application of ChB to anion recognition in solution is clearly an underdeveloped area of host–guest chemistry.[41] However, a recent investigation reported by Beer and collaborators have demonstrated the ability of halogen and chalcogen bonding based receptors to recognize anions in water.[42] The lack of progress in this area is likely due to the chemical instability of compounds containing the heavier chalcogen atoms, which are the ones exhibiting the most positive σ-holes. Herein, we report the design and synthesis of several sulfur, selenium and tellurium-based ChB binding motifs that allow us to analyze the association constants for ChB halide anion binding in the polar aprotic organic solvent THF. The energetic and geometric characteristics of the host-guest complexes have been also studied theoretically using DFT calculations and molecular electrostatic potential surface analysis. The influence of the Ch-atom on the binding energies and geometries has been also rationalized and it is found that for S-derivatives, the Ch-bonds are not competitive compared to H-bonds whilst Se and Te-derivatives exhibit higher tendency to form chalcogen bonding interaction with the anionic guests.

[a] Ms. Encarnación Navarro-García, Prof. Maria D. Velasco and Prof. A. Caballero *
Departmento de Química Orgánica
Universidad de Murcia
Campus del Espinardo, 30100 Murcia, Spain
E-mail: antocaba@um.es
[b] Mr. Bartomeu Galmés, and Prof. A. Frontera *
Department of Chemistry
Universitat de les Illes Balears
Crta. de Valldemossa km 7.5, 07122 Palma de Mallorca, Spain
E-mail: toni.frontera@uib.es

Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate))

10.1002/chem.201905786

We initially designed these receptors envisaging a possible cooperativity effect from an ancillary anion–π interaction due to the presence of the π-acidic surface, as shown in Scheme 1. However, both experimental and theoretical results indicate that a different binding mode operates in these systems due to the fact that the σ-hole opposite to the most electron-withdrawing group is more efficient (more positive electrostatic potential), as further described below and analyzed theoretically.



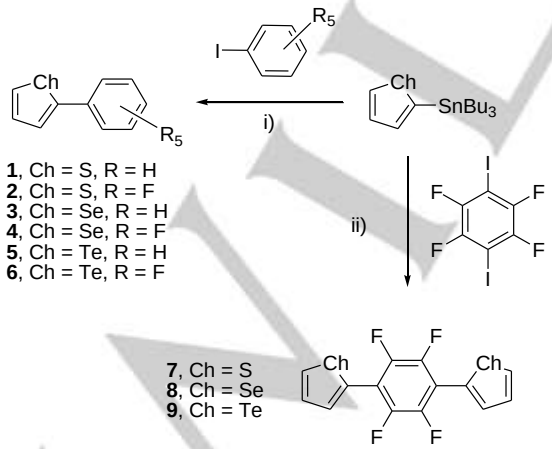
Scheme 1. Initially envisaged binding modes for the anion-complexes based on cooperative ChB and anion–π interactions

Results and discussion

Design and synthesis

The two families of ChB receptors used in this work are represented in Scheme 2. The first family comprises receptors **1–6** where only one ChB donor site is available. For this family we have used two types of aromatic rings (phenyl and pentafluorophenyl) to analyze the effect of their electronic nature on the binding constants. The second family is constituted by receptors **7**-**9** that are ditopic, so two concurrent ChBs can be established upon complexation. These two families of receptors allow us to analyze the influence of the Ch-atom on the anion-binding ability of the receptors in addition to the effect of the fluorination.

The Ch receptors **1–9** were synthesized via Stille coupling reaction by treating the previously synthesized 2-(tributylstannyl) -thiophene, -selenophene[43] or tellurophene[44] with the corresponding iodobenzene or iodoperfluorobenzene ring in the presence of the appropriate palladium catalysts (Scheme 2). Receptors **1–9** were obtained in good yields and were fully characterized using standard techniques: ^{1}H NMR, ^{13}C NMR and FAB mass spectrometry (see supporting information, Figures S1 to S69).



Scheme 2. Synthesis of the Ch receptors **1-9**. Reagents and conditions: i) catalyst: $Pd(PPh_3)_4$ or $Pd(PPh_3)_2Cl_2$. Solvents: THF, toluene or DMF, 3-72h. ii) $Pd(PPh_3)_4$, toluene, 2-6 days.

Anion binding studies

The anion binding properties of Ch receptors **1–9** were evaluated by ^{1}H NMR spectroscopy in the presence of several anions (Cl^-, Br^-, I^-, NO_3^-, AcO^-, $H_2PO_4^-$ and PF_6^-) added as tetrabutylammonium salts in CD_3CN. Additionally, ^{77}Se NMR or ^{125}Te NMR experiments were performed in the receptor bearing Se or Te atoms respectively.

The ^{1}H NMR spectra of receptors **1–9** exhibit the characteristic signals corresponding to the mono-substituted thiophene, -selenophene, or tellurophene rings, which appears as two doublet of doublets attributed to the Ha (δ = 7.36-9.33 ppm), Hb (δ = 7.37-8.34 ppm) and one multiplet asigned to the Hc (δ = 7.06-7.92 ppm) protons. Those signals are more downfield shifted when the molecular weight of the heteroatom increases and with the presence of the electron-withdrawing perfluorobenzene rings. In addition, receptors **1**, **3**, and **5** also showed the resonances attributed to the monosubstituted benzene at the aromatic region (δ = 7.20-7.63 ppm).

On the other hand, the ^{77}Se NMR or ^{125}Te NMR spectra of receptors **3** and **5** respectively showed a singlet at δ(**3**) = 590 ppm and δ(***5***) = 768 ppm while a triplet was observed in the perfluorobenzene derivatives at δ(**4**) = 661 ppm, δ(**6**) = 919 ppm, δ(**8**) = 660 ppm, δ(**9**) = 917 ppm.

Thus, addition of the aforementioned set of anions to solutions of the receptors **1–9** in tetrahydrofuran-d_8 showed that the presence of I^-, NO_3^-, AcO^-, $H_2PO_4^-$ and PF_6^- anions did not promote any changes in their ^{1}H NMR spectra even in a large excess On contrary, the presence of Cl^- and Br^- anions promotes important changes in their ^{1}H NMR.

Firstly, we analyze the Cl^- and Br^- binding behaviour of the monopodal receptors **1–6**. The addition of an increasing amount of Cl^- and Br^- anions to a solution of the receptors **1–6** in tetrahydrofuran-d_8 promotes an important and progressive downfield shift only in the resonance attributed to the acidic H–atom adjacent to the chalcogen atom Ha (Δδ = 0.06 – 0.14 ppm) indicating hydrogen bonding interaction of this proton with the anions. On the contrary, an upfield shift in the resonance of the proton Hc was observed. The resonance of the proton Hb was practically not modified by the presence of Cl^- and Br^- anions (Figure 1a). Some important information was obtained from the ^{77}Se NMR and ^{125}Te NMR titration experiments. It was not detected perturbation in the ^{77}Se NMR of the receptor **3**, bearing the benzene ring with the addition of both Cl^- (Figure 1b) or Br^- anion and therefore there are not evidences of the participation of the selenium atom in the binding event. Importantly, the downfield shift observed (Δδ = 2.71 ppm) in the signal of the ^{125}Te NMR spectrum of the analogous receptor **5** suggests the participation of the tellurium atom in the anion binding (Figure 1c).

The presence of the electron withdrawing pentafluorobenzene ring in the selenophene based receptor **4** causes the activation of the selenium atom. In contrast to the behaviour previously observed for receptor **3**, the addition of Cl^- and Br^- anion promotes a downfield shift (Δ***δ*** ~ 1.2 ppm) of the triplet present in the ^{77}Se NMR spectrum of the receptor **4**. The analogous tellurophene based receptor **6** shows two different behaviours, firstly, the addition of up to one equivalent of Br^- or Cl^- anion promotes the downfield shift of the triplet attributed to the tellurium

10.1002/chem.201905786

atom and the addition of more than one equivalent induces the upfield shift of this signal (Figure 2a). This behaviour is consistent with the recognition of two different anions with different binding modes.

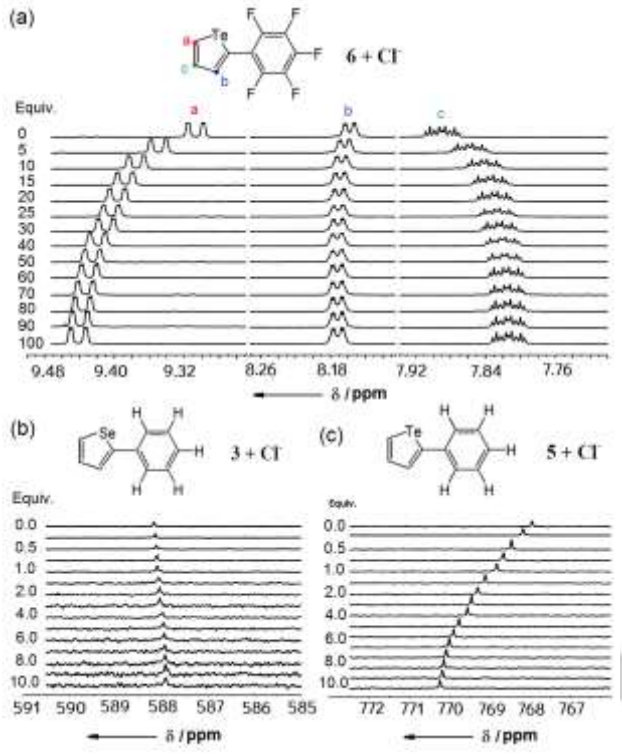


Figure 1. a) Changes in the ^{1}H NMR of the receptor **6** with the addition of Cl^{-} anion. b) Changes in the ^{77}Se NMR of the receptor **3** with the addition of Cl^{-} anion and c) Changes in the ^{125}Te NMR of the receptor **5** with the addition of Cl^{-} anion.

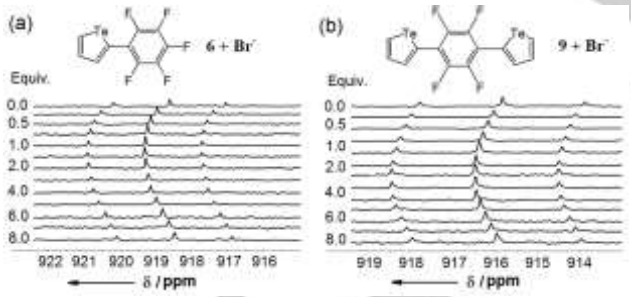


Figure 2. Changes in the ^{125}Te NMR of the receptor **6** (a) and **9** (b) with the addition of Br^{-} anion.

The same NMR titration experiments were also performed in the dipodal receptor **7**–**9**. The results were very similar to the obtained for the monopodal analogues **1**–**6**. Thus, ^{1}H NMR titration of the receptors **7**–**9**, upon addition of Cl^{-} and Br^{-}, clearly indicated the participation of the proton Ha solely in the anion-receptor binding, as was evidenced by the downfield shift of the signal attributed to the proton Ha ($\Delta\delta$ = 0.07-0.14 ppm) , while protons Hb and Hc were practically not perturbed. The downfield shift observed in the signals of the ^{77}Se NMR and ^{125}Te NMR spectra upon addition of Cl^{-} and Br^{-} anion to the receptors **8** and **9** also suggest an important contribution of the heteroatoms in the binding process. As was observed in the monopodal analogue **6**, two different processes were observed upon addition of Cl^{-} and Br^{-} anions to the dipodal receptor **9** (Figure 2b).

Taking into account the titration profiles obtained by the NMR experiment, the association constants were obtained by fitting the titration data to a 1:1 anion/receptor binding model in the thiophene and selenophene based receptors **1**–**4** and **7**–**8** and 2:1 anion/receptor binding model in the tellurophene based receptors **6** and **9** with use of the Dynafit program[45] and are collected in Table 1.

Table 1. Anion binding constants (K_{ass}, M^{-1}) of the Receptors **1**–**9** with Cl^{-} and Br^{-} anions at 298 K in tetrahydrofuran-d_8. The obtained errors are lower than 5%.

complex	K_{ass} (^{1}H-NMR)	K_{ass} (^{77}Se/^{125}Te-NMR)
1 + Cl^{-}	3.1	-
1 + Br^{-}	1.4	-
2 + Cl^{-}	3.5	-
2 + Br^{-}	2.2	-
3 + Cl^{-}	3.3	-
3 + Br^{-}	1.5	-
4 + Cl^{-}	3.6	7.2
4 + Br^{-}	3.0	5.6
5 + Cl^{-}	5.4	14.3
5 + Br^{-}	3.7	8.4
6 + Cl^{-}	K_1=78 K_2=6.5	No fitting
6 + Br^{-}	K_1= 20.8 K_2= 1.36	K_1=35.6 K_2=9.2
7 + Cl^{-}	5.5	-
7 + Br^{-}	3.7	-
8 + Cl^{-}	5.8	7.2
8 + Br^{-}	4.2	4.4
9 + Cl^{-}	K_1=51.1 K_2=5.0	No fitting
9 + Br^{-}	K_1=14.0 K_2=1.0	K_1=12.7 K_2=6.62

The association constants calculated for the thiophene (**1**, **2** and **7**) and selenophene (**3**, **4** and **8**) based receptors are noticeably lower than those obtained in tellurophene derivatives (**5**, **6** and **9**). On the other hand, the incorporation of pentafluorobenzene rings

10.1002/chem.201905786

causes a slight increase in the association constants with respect to the tetrafluorobenzene and also with the benzene derivatives. Finally, the chloride anion shows greater affinity for the receptors than the bromide anion.

MEP surface analysis

From the aforementioned titrations it is clear that the H-atom adjacent to the chalcogen atom in the five membered ring actively participates in the binding mechanism. This strongly disagrees with a binding mode where the anion is located over the aromatic ring, as shown in Scheme 1, since this H-atom would be not affected during the titrations. We have started the theoretical analysis by computing the molecular electrostatic potential (MEP) surfaces of the receptors (see ESI for the computational methods). The isosurface used for the MEP plots shown in Figures 3–6 is 0.001 a.u., which is the best estimate of the van der Waals surface. However, for a set of receptors (**1**–**6**) we have also plotted the MEP surfaces using two additional isosurfaces (0.002 and 0.0005 a.u.) that are represented in Figures S70 and S71 (see ESI). Remarkably, the trends in the MEP values are the same, thus giving reliability to the analysis commented below.

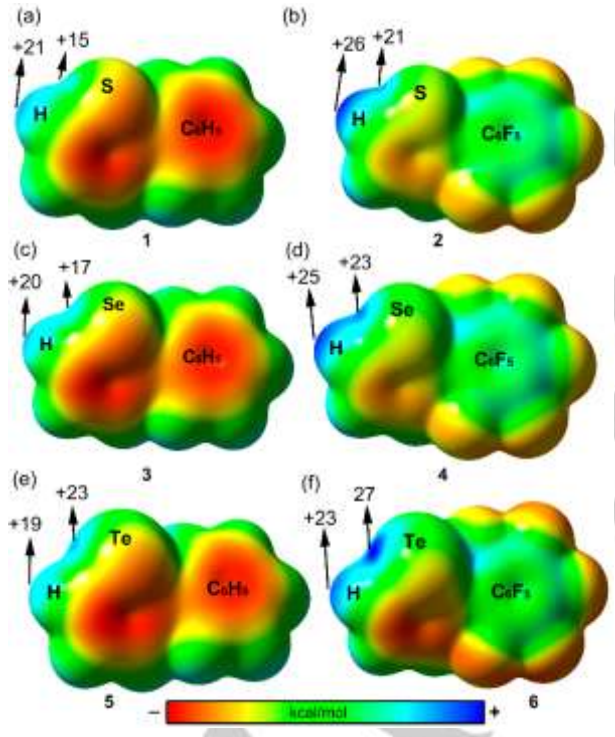


Figure 3. MEP surfaces of **1** (a) **3** (c) and **5** (e) monopodal phenyl receptors and **2** (b) **4** (d) and **6** (f) monopodal pentafluorophenyl receptors. The MEP values at selected points of the surfaces are indicated in kcal/mol. Isosurface 0.001 a.u.

The optimized structures of the monopodal receptors **1**–**6** are shown in Figure S72 (ESI) and the MEP surfaces in Figure 3. Some interesting issues can be deduced from the MEP surface plots. First, for receptors with S and Se, the MEP values at the H-atom adjacent to the chalcogen atom presents more positive MEP value than that at the σ-hole of the chalcogen atom. In contrast, for Te, the maximum MEP is located at the σ-hole. Therefore, different binding mode can be anticipated. Second, as expected the receptors with the pentafluorophenyl ring exhibit more positive values of MEP both at the σ-hole and the H-atom than those with the phenyl ring. As shown in Figure S72, the dihedral angle between the aromatic rings is around 30º for all receptors. In this conformation the second σ-hole at the chalcogen atom is not accessible, as shown in Figure 3.

Therefore, for the pentafluorophenyl derivatives, we have also computed the MEP surfaces using a perpendicular conformation between both rings, in order to examine the influence of the C–C dihedral angle on the MEP values (see Figure 4).

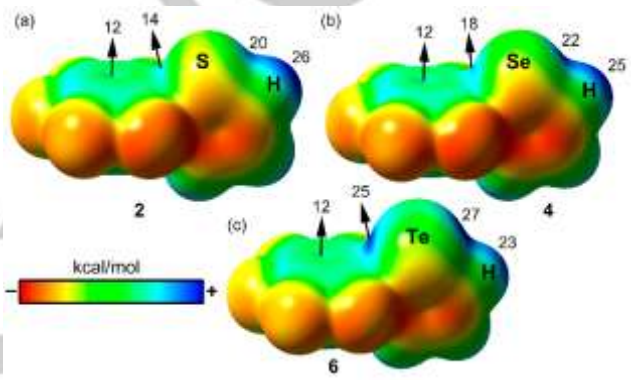


Figure 4. MEP surfaces of **2** (a) 4 (b) and **6** (c) monopodal receptors using a C–C rotational angle of 90^0. Isosurface 0.001 a.u.

This conformation is expected for the complexes where the anion interacts with the receptor using a combination of ChB and anion–π interactions. Interestingly, the σ-hole that points toward the aromatic ring is hidden in S and Se receptors **2** and **4**. Moreover, the maximum of MEP is located at the H-atom that is adjacent to the Ch-atom. The MEP analysis also shows that the Te derivative **6** presents similar values at both σ-holes (see Figure 4c). Overall, the MEP surface analysis indicates that the anion will have a preference for the interaction with both the H-atom and the chalcogen's σ-hole simultaneously rather than the anion–π and ChB combination, especially taking into consideration that, at the PBE0-D3(THF)/def2-TZVPP level of theory, the perpendicular conformation is 1.2 kcal/mol less stable than the minimum in all three receptors. Moreover, this MEP surface analysis strongly agrees with the NMR titrations commented above, since the H-atom in alpha to the Ch-atom is strongly affected by the addition of the anion and, for S and Se receptors, the MEP is maximum at these H-atoms. Moreover, for the Te receptor the MEP maximum is located at the σ-hole, also in agreement with the ^{125}Te NMR experiments shown in Figure 2.

For the dipodal receptors **7**–**9** (see Figure S73 for the optimized geometries) we have also computed the MEP surfaces using two conformations: (i) the global minima (Figure 5) that exhibit dihedral angles between the rings ranging 15–17º and, (ii) fixed

10.1002/chem.201905786

conformations (see Figure 6) with dihedral angles fixed at 90º and with both five membered rings in a *syn* arrangement (see Scheme 1 right). In this conformation the anion would interact with the receptor by means of a combination of ChB and anion–π interactions. The MEP surfaces gathered in Figures 5 and 6 show that the trends are similar to those previously described for the monopodal receptors.

The σ-hole is imperceptible for the S-derivative in any of both conformations and the positive MEP value at the adjacent H-atom is significantly larger. For Se, the σ-hole is visible but also smaller than that at the H-atom. Finally, the Te derivative presents the largest and most intense σ-hole and it is the only one where the MEP value at the H-atom is smaller than that at the Ch-atom. It is worth emphasizing that the K_{ass} values of Te-complexes with Cl^- and Br^- are larger for the monopodal than dipodal receptors (see Table 1), in line with the higher value of MEP at the σ-hole of the monopodal receptor. This is likely due the stronger electron withdrawing ability of the C_6F_5 group compared to the C_6F_4 one.

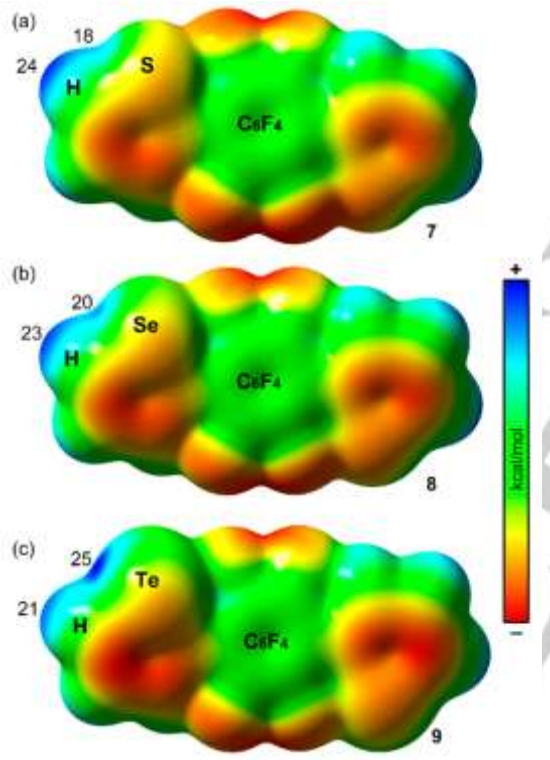


Figure 5. MEP surfaces of **7** (a) **8** (b) and **9** (c) dipodal receptors. The MEP values at selected points of the surfaces are indicated in kcal/mol. Isosurface 0.001 a.u.

It is worth mentioning that for the Te receptor in the perpendicular conformation, the MEP surface analysis shows that the most favored binding mode should be the anion–π and two concurrent ChBs, since the π-hole is accessible and of similar magnitude to that pointing to the exterior of the cavity. Even though the energy cost for rotating both tellurophene rings in THF is 3.3 kcal/mol, this binding mode should be competitive. However, the experimental ^{1}H-NMR results commented above evidence that the H-atom participates in the binding mechanism, that rule out the formation of the combined anion–π/ChB complex. This aspect is further studied below.

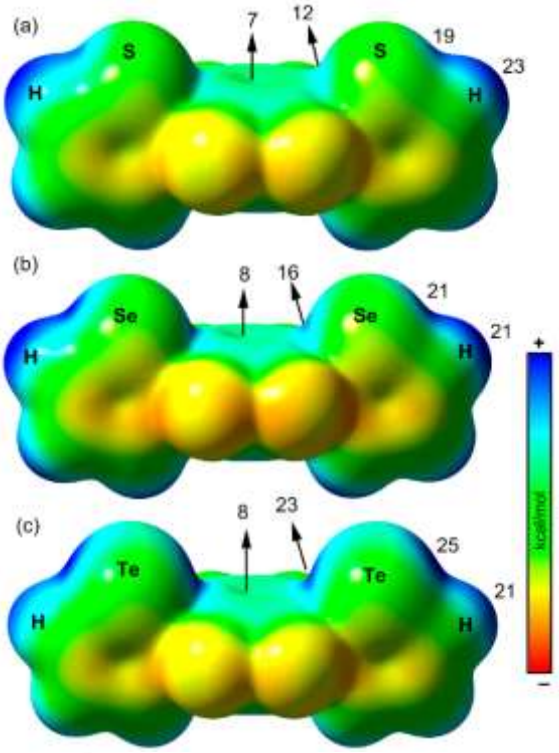


Figure 6. MEP surfaces of S, (a) Se (b) and Te (c) dipodal receptors. The MEP values at selected points are indicated in kcal/mol. Isosurface 0.001 a.u.

Geometric and energetic analysis

We have optimized the geometries and calculated the binding energies of chloride and bromide complexes with receptors **1**–**9**, (see ESI for details). Figure 7 shows the geometries for the complexes of the first family of receptors interacting with Cl^- anion and those involving bromide are included in the ESI (Figure S74). It can be observed that all Cl^- complexes exhibit very modest interaction energies, in agreement with the small association constants. Interestingly, the H-bonding distance increases and the Ch-bond distance decreases on going from the lighter to the heavier chalcogen atom, in good agreement with the MEP surface analysis. That is, the relative importance of the σ-hole interaction increases on going from S to Te. Moreover, the binding energies obtained for the fluorinated receptors are larger in absolute value than those corresponding to the non-fluorinated ones, also in agreement with the MEP analysis and experimental association constants (see Table 1).

Figure 8 shows some representative complexes of the second family of receptors interacting with Cl^- and Br^- anions (the rest is included in the ESI, Figure S75). It can be observed that the complexes where the anion interacts via HB and ChB interactions (Figure 8a,b) are energetically favored with respect to those where the anion is located inside the cavity, which is forming two

10.1002/chem.201905786

concurrent ChBs and the ancillary anion–π interaction (Figure 8c,d).

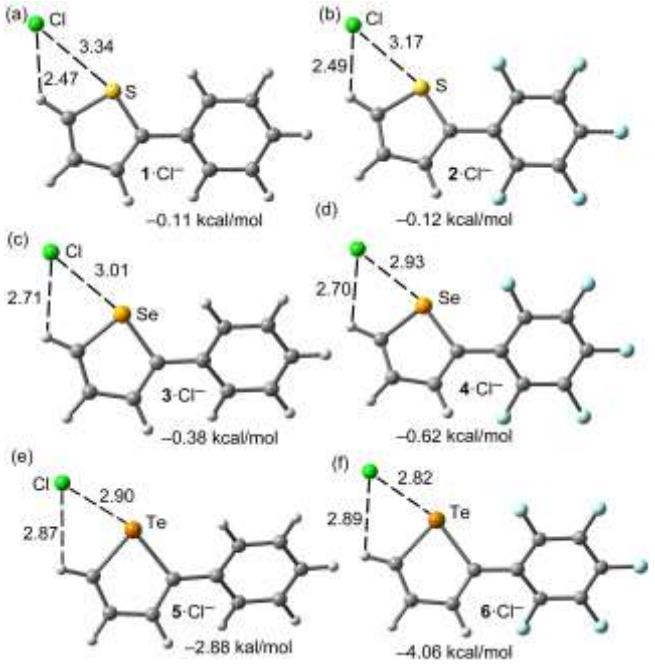


Figure 7. PBE0-D3/def2-TZVPP optimized geometries of monopodal complexes with Cl^-. Distances in Å. BSSE-corrected energies in THF.

In fact, this binding mode is not favored for Br^- exhibiting a positive interaction energy, evidencing that the receptor is not able to desolvate the anion. It can be observed that the ChB distances are quite longer in these complexes, thus explaining the less favorable binding energies. Moreover, in these ChBs/anion–π complexes, there is a deformation of the receptor since the exocyclic C–C bonds are bent toward the anion in an attempt to reinforce the ChBs (see Figure 8c,d). It is interesting to note that the binding energies of dipodal receptor **9**·(Ch = Te, fluorinated) with Cl^- and Br^- are weaker than those obtained for monopodal receptor **6** (Ch = Te, R = F) in good agreement with the experimental association constants (see Table 1).

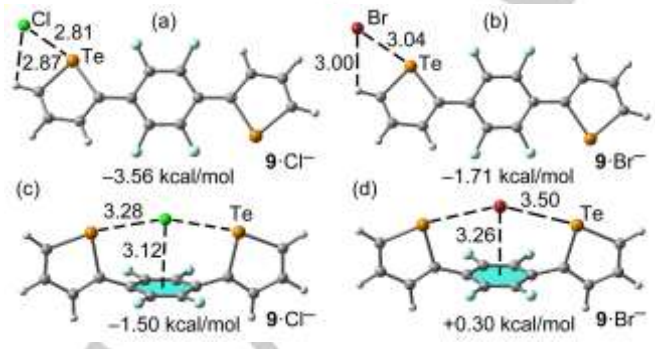


Figure 8. PBE0-D3/def2-TZVPP optimized geometries for two different binding modes in dipodal complexes with Cl^- (a,c) and Br^- (b,d). Distances in Å. BSSE-corrected energies in THF.

Finally, we have also explored the possibility of the formation of complexes with 2:1 anion/receptor stroichiometry for the complexation of bromide with receptors **9**, since the fitting of the experimental data suggests the incorporation of two anions in the tellurophene based receptor. Agreeably, we have found two possible binding modes corresponding to 2:1 complex that are represented in Figure 9. One of both is symmetric and each Br forms concurrent hydrogen and chalcogen bonds. The other one is energetically more favored and each Br^- interacts with the receptors in a different manner. That is, one Br^- is bonded combining Ch-bonding and anion–π interaction and the other one simply interacts with the tellurophene establishing a H-bonding interaction with Ha.

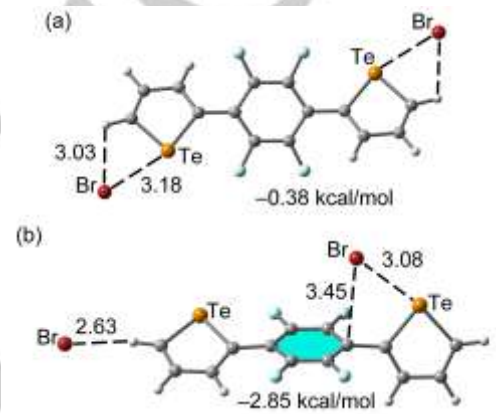


Figure 9. (a,b) PBE0-D3/def2-TZVPP optimized geometries for two different binding modes for receptor **9** interacting with Br^-. Distances in Å and BSSE-corrected energies in THF.

Conclusions

In conclusion, we have prepared two families of sulfur, selenium and tellurium-based ChB-donor motif capable of binding chloride and bromide in THF. These families of receptors have allowed us to analyze the effect of the chalcogen atom on the association constants and also competition between H-bonding and chalcogen bonding interactions. For the S and Se the HB interactions are quite competitive whilst for tellurium the ChB dominates. The comprehensive DFT study and especially the MEP surface analysis allowed us to rationalize the experimental findings since the ^{1}H, ^{77}Se and ^{125}Te-NMR shifts agree well with the MEP values at the σ-holes in H and Ch atoms of thiophene, selenophene and tellurophene rings. These findings are expected to be useful in the nascent field of molecular recognition of anions based on neutral ChB donors, especially for those researchers in the field working on the integration of ChB donor motifs into receptors for molecular recognition and catalysis. Finally, future directions of this work are the utilization of oxoanions, the analysis of atropoisomerism in the receptors and to block the acidic H-atom with appropriate *alpha* substituents on the heterocycles.

Acknowledgements

We thank the MICIU/AEI (project CTQ2017-85821-R, RED2018-102331-T and CTQ2017-86775-P FEDER funds) and the Fundación Séneca Región de Murcia (CARM) (project 20819/PI/18) for financial support. We thank the CTI (UIB) for computational facilities.

Keywords: Chalcogen bonding • Supramolecular Chemistry • Anion-receptors • MEP analysis • DFT study

References

[1] H. J. Schneider, *Angew. Chem. Int. Ed.* **2009**, *48*, 3924–3977.
[2] J. M. Lehn in *Supramolecular chemistry concepts and perspectives*, Wiley-VCH, Weinheim, **1995**.
[3] J. W. Steed, J. L. Atwood in *Supramolecular chemistry*, Wiley, Chichester, **2000**.
[4] G. Gilli, P. Gilli, The Nature of the Hydrogen Bond, Oxford University Press, Oxford, **2009**.
[5] G. R. Desiraju, T. Steiner, The Weak Hydrogen Bond in Structural Chemistry and Biology, Oxford, New York, **1999**.
[6] S. Scheiner, Hydrogen Bonding. A Theoretical Perspective, Oxford University Press, New York, **1997**.
[7] S. J. Grabowski in Hydrogen Bonding—New Insights, Springer, Amsterdam, **2006**.
[8] G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimagi, G. Resnati, G. Terraneo, *Chem. Rev*. **2016**, *116*, 2478–2601
[9] P. Scilabra, G. Terraneo, G. Resnati, *Acc. Chem. Res.* **2019**, *52,* 1313-1324
[10] S. Scheiner, *Acc. Chem. Res*. **2013**, *46*, 280-288
[11] (a) A. Bauzá, T. J. Mooibroek, A. Frontera, *Angew. Chem. Int. Ed*. **2013**, *52*, 1231 7–12321; (b) A. Bauzá, S. K. Seth, A. Frontera, *Coord. Chem. Rev*. **2019**, 384, 107-125.
[12] (a) A. Bauzá, A. Frontera, *Angew. Chem. Int. Ed.* **2015**, *54*, 7340–7343; (b) A. Bauzá, A. Frontera, *Coord. Chem. Rev*. **2020**, *404*, 213112
[13] S. Grabowski, *J. Comput. Chem*, **2018**, *39*, 472-480
[14] P. Politzer, J. S. Murray, *Crystals* **2017**, *7*, 212– 226
[15] J. S. Murray, P. Lane, T. Clark, K. E. Riley, P. Politzer, *J. Mol. Model.* **2012**, *18*, 541–548.
[16] G. Cavallo, P. Metrangolo, T. Pilati, G. Resnati, G. Terraneo,. *Cryst. Growth Des*. **2014**, *14*, 2697– 2702
[17] (a) A. Bauzá, T. J. Mooibroek, A. Frontera, *ChemPhysChem* **2015**, *16*, 2496–2517; (b) A. Bauza, A. Frontera, *ChemPhysChem* **2020**, *21*, 26–31.
[18] D. J. Pascoe, K. B. Ling, S. L. Cockroft, *J. Am. Chem. Soc*. **2017**, *139*, 15160– 15167.
[19] S. Scheiner, *Chem. Eur. J*. **2016**, *22*, 18850– 18858.
[20] J. Y. C. Lim, P. D. Beer, *Chem* **2018**, *4*, 731– 783.
[21] C. B. Aakeroy, D. L. Bryce, G. R. Desiraju, A. Frontera, A. C. Legon, F. Nicotra, K. Rissanen, S. Scheiner, G. Terraneo, P. Metrangolo, G. Resnati, *Pure. Appl. Chem*. **2019**, *91*, 1889–1892
[22] D. J. Pascoe, K. B. Ling, S. L. Cockroft, *J. Am. Chem. Soc*. **2017**, *139*, 15160−15167.
[23] C. C. Robertson, R. N. Perutz, L. Brammer, C. A. Hunter, *Chem. Sci*. **2014**, *5*, 4179−4183.
[24] J. Fanfrlk, A. Prda, Z. Padelkov, A. Pecina, J. Machcek, M. Lepsk, J. Holub, A. Ruzicka, D. Hnyk, P. Hobza, *Angew. Chem. Int. Ed*. **2014**, *53*, 10139–10142.
[25] (a) Y. Zhang, W. Wang, *Crystals* **2018**, *8*, 163; (b) A. Bauza, A. Frontera, *Molecules* **2018**, *23*, 699; (c) A. Franconetti, D. Quiñonero, A. Frontera, G. Resnati, *Phys. Chem. Chem. Phys*. **2019**, *21*, 11313-11319; (d) B. Galmés, A. Juan-Bals, A. Frontera, G. Resnati, *Chem. Eur. J*. **2020**, *26*, DOI: 10.1002/chem.201905498
[26] Y. Nagao, T. Hirata, S. Goto, S. Sano, A. Kakehi, K. Iizuka, M. Shiro, *J. Am. Chem. Soc*. **1998**, *120*, 3104–3110.
[27] S. Benz, J. López-Andarias, J. Mareda, N. Sakai, S. Matile, *Angew. Chem. Int. Ed*. **2017**, *56*, 812–815.
[28] S. Benz, J. Mareda, C. Besnard, N. Sakai, S. Matile, *Chem. Sci*. **2017**, *8*, 8164–8169.
[29] P. Wonner, L. Vogel, M. Deser, L. Gomes, F. Kniep, B. Mallick, D. B. Werz, S. M. Huber, *Angew. Chem. Int. Ed*. **2017**, *56*, 12009–12012.
[30] (a) L. M. Lee, M. Tsemperouli, A. I. Poblador-Bahamonde, S. Benz, N. Sakai, K. Sugihara, S. Matile, *J. Am. Chem. Soc*. **2019**, *141*, 2, 810-814; (b) G. Sanchez-Sanz, C. Trujillo, *J. Phys. Chem. A*, **2018**, *122*, 1369-1377.
[31] (a) P. C. Ho, P. Szydlowski, J. Sinclair, P. J. W. Elder, J. Kebel, C. Gendy, L. M. Lee, H. Jenkins, J. F. Britten, D. R. Morim, I. Vargas-Baca, *Nat. Commun*. **2016**, *7*, 11299.; (b) L. Chen, J. Xiang, Y. Zhao, Q. Yan, *J. Am. Chem. Soc*. **2018**, *140*, 7079 – 7082.
[32] K. T. Mahmudov, M. N. Kopylovich, M. F. C. Guedes da Silva, A. J. L. Pombeiro, *Dalton Trans*. **2017**, *46*, 10121–10138.
[33] (a) J. Y. C. Lim J. Y. Liew, P. D. Beer, *Chem. Eur. J*. **2018**, *24*, 14560–14566; (b) G. E. Garrett, E. I. Carrera, D. S. Seferos, S. Taylor, *Chem. Commun*. **2016**, *52*, 9881-9884
[34] N. A. Semenov, A. V. Lonchakov, N. A. Kushkarevsky, E. A. Suturina, V. V. Korolev, E. Lork, V. G. Vasiliev, S. N. Konchenko, J. Beckmann, N. P. Gritsan, A. V. Zibarev, *Organometallics*, **2014**, *33*, 4302–4314.
[35] G. E. Garrett, G. L. Gibson, R. N. Straus, D. S. Seferos, M. S. Taylor, *J. Am. Chem. Soc*. **2015**, *137*, 4126–4133
[36] V. Kumar, C. Leroy, D. L. Bryce, *CrystEngComm*, **2018**, *20*, 6406-6411
[37] (a) A. F. Cozzolino, P. J. W. Elder, I. Vargas-Baca, *Coord. Chem. Rev*. **2011**, *255*, 1426 –1438; (b) A. Kremer, A. Fermi, N. Biot, J. Wouters, D. Bonifazi, *Chem. Eur. J*., **2016**, *22*, 5665 –5675.
[38] A. Mishra, C.-Q. Ma, P. Bäuerle, *Chem. Rev*. **2009**, *109*, 1141–1276.
[39] M. E. Brezgunova , J. Lieffrig , E. Aubert , S. Dahaoui , P. Fertey , S. Lebègue , J. Angyan , M. Fourmigué, E. Espinosa, *Cryst. Growth Des*. **2013**, *13*, 3283–3289.
[40] P. Wonner, L. Vogel, M. Düser, L. Gomes, F. Kniep, B. Mallick, D. B. Werz, S. M. Huber, *Angew. Chem. Int. Ed*., **2017**, *56*, 12009–12012.
[41] (a) L. Brammer, *Faraday Discuss*., **2017**, *203*, 485–507; (b) A. Lari, R. Gleiter, F. Rominger, *Eur. J. Org. Chem*., **2009**, 2267–2274; (c) S. Scheiner, *Faraday Disc*, **2017**, *203*, 213–226.
[42] A. Borissov, I. Marques, J. Y. C. Lim, V. Félix, M. D. Smith, P. D. Beer, *J. Am. Chem. Soc*. **2019**, *141*, 9, 4119-4129.
[43] J-H Kim, J. B. Park, S. A. Shin, M. H. Hyun, D-H Hwang. *Polymer.* **2014**, *55*, 3605-3613.
[44] P. Data, M. Lapkowski, R. Motyka, J. Suwinski.*Electrochim. Acta*. **2012**, *83*, 271-282.
[45] P. Kuzmic, *Anal. Biochem*., **1996**, *237*, 260–273.

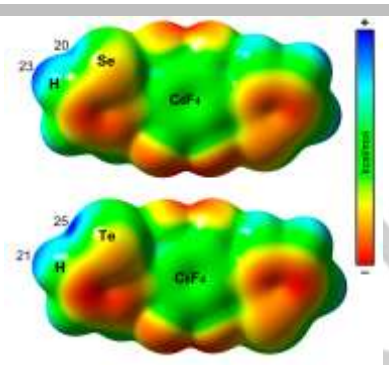
10.1002/chem.201905786

WILEY-VCH

Entry for the Table of Contents

FULL PAPER

The synthesis of three new families of sulfur, selenium and tellurium-based ChB binding motifs is reported herein. The stability of the chalcophene binding motifs has enabled the determination of association constants for ChB halide anion binding in the polar aprotic solvent THF by ^{1}H-, ^{77}Se- and ^{125}Te-NRM experiments.



E. Navarro-García,[a] B. Galmés,[b] M. D. Velasco[a], A. Frontera[b], and A. Caballero[a],**

Page No. – Page No.

Anion recognition by neutral chalcogen bonding receptors: experimental and theoretical investigation