# A DFT Study of Tin- and Crown-Ether-Based Host Molecules Capable of Binding Anions and Cations Simultaneously

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DFT calculations are reported for a series of tin- and crown-ether-based host compounds {i.e., the trimethyl derivatives [18]-crown-6-$C_6H_3COOSn(CH_3)_3$ and [15]-crown-5-$C_6H_3COOSn(CH_3)_3$} capable of binding cations and anions simultaneously. The B3LYP functional together with the 6-31G* basis set was used for the atoms C, H, N, O, S, Na and K and the 3-21G* basis set for Sn in order to obtain insights into the factors determining the nature of the interactions of these compounds with the neutral molecules acetone and $H_2O$, the $SCN^-$ anion, and the $Na^+$ and $K^+$ cations. The interaction strength pattern with these molecules was explained by the use of a series of reactivity descriptors such as the Fukui function, hardness, local softness, and the MEP (molecular electrostatic potential). In all cases studied in this paper, the complexes with $Na^+$ were more stable than those with $K^+$, correlating with the size of the cation and the volume available in the crown ether. Moreover, this finding is also in accordance with the greater hardness of $Na^+$ relative to $K^+$, in combination with the hard environment of the crown ether moiety. This region was also analysed by computation of electrostatic potentials, which showed that highly negative values are associated with the inside region of the cavity of the crown, this region thus being amenable to electrophilic attack. The HSAB principle, characterising the reactive sites on the basis of local softness and the Fukui function, provided a firm explanation of the reactivity of the tin atom of the crown ether benzocarboxylate towards $SCN^-$, acetone and water. The HSAB concept was also successfully used to explain the preference of the tin atoms in both crown ethers to bind with the nitrogen atom rather than the sulfur atom of $SCN^-$. This result is a confirmation that the tin atoms in the compounds under consideration behave as hard atoms. Overall, these results fit remarkably well with previous experimentally measured NMR spectroscopy data and demonstrate that the interactions of this kind of molecules can be predicted and interpreted by the use of DFT calculations and DFT-based reactivity descriptors, as well as MEP calculations.



## 1. Introduction

The complexation of host molecules capable of binding an anion and a cation simultaneously is still a relatively unexplored topic in chemistry.[1] Numerous studies, however, have been devoted either to the interactions between cations and preorganised host molecules,[2] or to fixation of anions by neutral molecules containing Lewis acidic metal centres.[3] Studies on interactions between crown ethers and various inorganic and organic cations have spawned wide applications in chemistry, biology, medicine and technology,[4] while the Lewis acidity of the tin atom in, for instance, organotin halides is well documented.[5] Fewer studies have been reported on interactions of Lewis bases with organotin carboxylates,[6] despite widespread interest in their in vitro antitumour activity[7] and their rich structural diversity in the solid state.[8]

We recently reported a novel type of salt complexation by a new class of host molecules, containing both a crown ether susceptible to interaction with the cation and a Lewis acidic tin centre potentially acting as an anion carrier.[9] It was demonstrated that tri-*n*-butyl and triphenyltin derivatives of 4-carboxybenzo-[18]crown-6 or [15]crown-5 are receptors capable of binding $M^+SCN^-$ ion pairs heterotopically. The Lewis acidic complexation of Sn by the thiocyanate anion cooperates with the crown ether complexation by the alkali metal cation and gives rise to a large charge separation, as evidenced by X-ray data in the crystalline state for the triphenyltin derivatives and by NMR spectroscopic data in solution for the tri-*n*-butyltin analogues.

This paper presents a theoretical investigation of the trimethyltin analogues of these compounds {i.e., [18]crown-6-$C_6H_3COOSn(CH_3)_3$ and [15]crown-5-$C_6H_3COOSn(CH_3)_3$,

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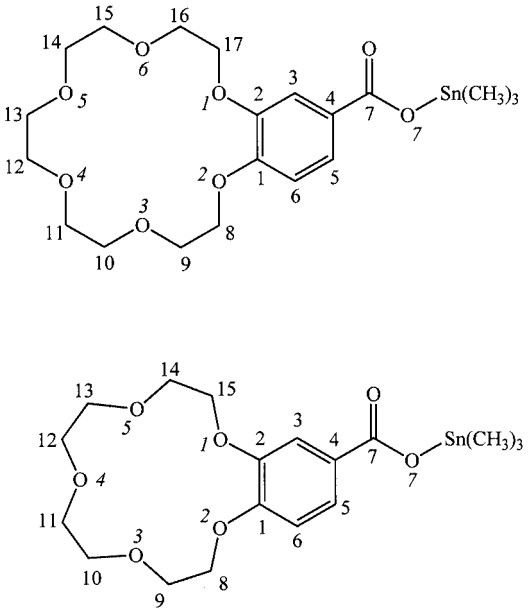



Figure 1. Molecular structures of [18]crown-6-$C_6H_3COOSn(CH_3)_3$ and [15]crown-5-$C_6H_3COOSn(CH_3)_3$

see Figure 1, the triphenyltin and tributyltin analogues being computationally too time-consuming}, in order to gain more insight into the factors determining the nature of the interactions of these molecules with the $SCN^-$ anion and the $Na^+$ and $K^+$ cations. Moreover, as far as the inductive effects of the functional groups attached to the tin atom are concerned, the methyl group lies in between the +I *n*-butyl group and the −I phenyl group, and so also constitutes an optimal choice from that point of view. The studies were performed at a nonempirical ab initio level, still relatively rare for tin-containing compounds,[10] and interpreted by the use of DFT-based descriptors and principles.

Of particular interest in the understanding of chemical reactivity are the so-called response functions of the system to perturbations in the number of electrons or external potential, commonly referred to as atomic or molecular reactivity descriptors.[11−17] These descriptors have a sound basis in density functional theory (DFT).[18] Electronic chemical potential (μ), electronegativity (χ), hardness (η) and softness (*S*) are examples of such reactivity descriptors (for detailed accounts see refs.[18b−18d]). In this work, the basic quantities to be addressed are hardness and softness both at the global (i.e., molecular) and at the local (i.e., atomic sites in molecules) levels. A detailed discussion of these quantities can be found elsewhere.[18−24]

The local properties[18] developed are the Fukui function (FF) and the local softness typically describing the local role of a specific atom within a molecule in the reactivity of the latter.[18]

Fukui function and local softness, which are related to changes in the electron density function $\rho(r)$ with the total number of electrons at constant external potential $[\partial\rho(r)/\partial N]_v$, have been used to determine the site of reactivity of a system.[25] The FF was originally used essentially as an indicator of intramolecular reactivity sequences[26] (regioselectivity), the local softness being involved in intermolecular reactivity sequences. When the HSAB principle is used at a local level, the consideration of local softness turns out to be essential for estimating relative interaction energies of different sites in a molecule towards electrophilic or nucleophilic reagents.

In this study, and also in the context of a series of papers aiming at the description of properties of tin compounds with the aid of DFT reactivity indicators,[27−28] we investigate the use of the FF and the local softness to describe the interactions between the tin atom and the $SCN^-$ anion, as well as neutral molecules such as acetone for which experimental NMR spectroscopic data are available,[9] Pearson's hard and soft acids and bases (HSAB) principle[19−21] being expected to act as the guiding principle.[29,30] When the HSAB principle is applied in a local sense,[31] regioselectivity problems can be addressed on the basis of the idea that soft (or hard) regions of one reaction partner will preferentially interact with soft (or hard) regions of the other partners.[32−34] We are also interested in knowing whether (i) only the cation or the anion is involved in a monotopic interaction, or (ii) both ions are involved in a heterotopic interaction.[1k] If the latter holds, an additional question is whether anions and cations remain electrostatically paired or undergo a charge separation from their initial ion pair.

The molecular electrostatic potential (MEP) is also used to predict the behaviour of the crown ether moiety, because its cavity is expected to be hard, as it is found to interact with hard cations such as $Na^+$ and $K^+$.

The MEP[35−37] has indeed been found suitable for the description of electrostatic (i.e., nonorbital-based) interactions, and has been used in recent years to study the structures and reactivities of polyoxometallate cages and, in our group, the $(CH_3Sn)_{12}O_{14}(OH)_6^{2+}$ cationic cluster.[28] The spatial distribution and the values of the MEP can be taken, at least in the case of a fairly hard reagent, as an indicator of where a nucleophilic or electrophilic attack is likely to take place. We used MEP calculations to describe the interactions between the oxygen atoms of the crown ether and $Na^+$ and $K^+$ cations.

## 2. Theory and Computational Details

As a detailed presentation and discussion of the reactivity parameters used in this paper can be found elsewhere,[18,38] only the relevant expressions used for the evaluation of different quantities for the crown ethers [15]crown-5-$C_6H_3COOSn(CH_3)_3$ and [18]crown-6-$C_6H_3COOSn(CH_3)_3$ are given here.

The global hardness (η) and the global softness (*S*) are calculated from Equations (1) and (2), by use of the finite-difference approximation, where *IE* and *EA* are the vertical ionisation energy and electron affinity, respectively.

$$\eta = \frac{IE - EA}{2} \quad (1)$$

$$S = \frac{1}{2\eta} \tag{2}$$

The Fukui function $f(r)$ is defined as the partial derivative of the total electron density at a given point $r$, $\rho(r)$, with respect to the number of electrons $N$, at constant external potential $v(r)$ (the potential exerted by the nuclei) determined for the $N$ values considered. Parr and Yang[18,19,25] have proposed an association of different reactivity indices through Equation (3).

$$f(\underline{r}) = \left(\frac{\partial \rho(\underline{r})}{\partial N}\right)_{v(\underline{r})} \tag{3}$$

The expressions used to investigate nucleophilic or electrophilic attack on the system are given by Equation (4) for a nucleophilic attack and Equation (5) in the case of an electrophilic attack.

$$f^{+}(\underline{r}) = \left(\frac{\partial \rho(\underline{r})}{\partial N}\right)^{+}_{v(\underline{r})} \tag{4}$$

$$f^{-}(\underline{r}) = \left(\frac{\partial \rho(\underline{r})}{\partial N}\right)^{-}_{v(\underline{r})} \tag{5}$$

The superscripts + and − refer to right and left derivatives, respectively. In a finite difference approach, $f^{+}(r)$ and $f^{-}(r)$ can be approximated by Equations (6) and (7),[18,25,39] where $\rho_N$, $\rho_{N+1}$ and $\rho_{N-1}$ are the electron densities of the systems with $N$, $N + 1$ and $N - 1$ electrons, respectively.

$$f^{+}(\underline{r}) \approx \rho_{N+1}(\underline{r}) - \rho_{N}(\underline{r}) \tag{6}$$

$$f^{-}(\underline{r}) \approx \rho_{N}(\underline{r}) - \rho_{N-1}(\underline{r}) \tag{7}$$

Because of the constraint of a constant external potential, the quantities $\rho_{N+1}$ and $\rho_{N-1}$ are calculated with the same geometry as the $N$ electron system.

The $f^{o}$ function, which governs radical attack, is considered to be the average of $f^{+}(r)$ and $f^{-}(r)$, and can therefore be approximated by Equation (8).

$$f^{o}(\underline{r}) \approx \frac{1}{2}[\rho_{N+1}(\underline{r}) - \rho_{N-1}(\underline{r})] \tag{8}$$

Yang and Mortier[26] have also proposed a condensed version of Equations (6) to (8). The information contained in $f(r)$ in the neighbourhood of a given atom A can be approximated by use of the atomic population $N_A$, obtained by population analysis on the considered atom.[40] Accordingly, the condensed Fukui function on the atom A, $f_A$, is obtained as Equations (9) to (11), where $N_A(N)$ stands for the atomic population on atom A in the $N$ electron system.

$$f_A^{+} \approx N_A(N+1) - N_A(N) \tag{9}$$

$$f_A^{-} \approx N_A(N) - N_A(N-1) \tag{10}$$

$$f_A^{o} \approx \frac{1}{2}[N_A(N+1) - q_A(N-1)] \tag{11}$$

According to the relation given in Equation (12) the corresponding condensed local softness parameters can easily be calculated from the condensed Fukui function and the global softness, as in Equation (13).

$$s(\underline{r}) = Sf(\underline{r}) \tag{12}$$

$$s_A^{+} = Sf_A^{+} \tag{13}$$

The MEP,[36,37] $V(r)$, was calculated in the usual way, neglecting polarisation and nuclear rearrangement effects, as described in Equation (14), where the summation runs over all nuclei A with charge $Z_A$ and coordinate $R_A$.

$$V(\underline{r}) = \sum_A \frac{Z_A}{|\underline{R}_A - \underline{r}|} - \int \frac{\rho(\underline{r}')}{|\underline{r}' - \underline{r}|} d\underline{r}' \tag{14}$$

The first term on the right-hand side of Equation (14) gives the contribution of the nuclei, the second term reflects the effect of the electrons.

In this contribution, the MEP has been computed in a plane containing three oxygen atoms (oxygen O1, O2 and O3; see Figure 1) of the crown ether moiety, for both the [18]crown-6 and the [15]crown-5 systems (see Figures 3 and 4, respectively). The MEP was also calculated on a straight line perpendicular to the plane containing the oxygen atoms used to calculate the MEP contours, starting at 5 Å above and ending 5 Å below the mean crown ether plane, with steps of 0.01 Å.

Structures and energies were calculated with the aid of the Gaussian98[41] program. All geometries were completely optimised at the DFT level with the B3LYP[42−44] functional, with a 6-31G*[45] basis set for H, C, O, Na and K and 3-21G*[45] for Sn.

The geometries of all the complexes between the tin atoms of the crown ether derivatives and the nucleophiles ($SCN^{-}$, acetone and water) interacting with the tin atom, and the cations ($Na^{+}$ and $K^{+}$) interacting with the crown ether moiety itself were fully optimised.

## 3. Results and Discussion

The stabilisation energies resulting from the interactions between [15]crown-5-$C_6H_3COOSn(CH_3)_3$ and [18]crown-6-

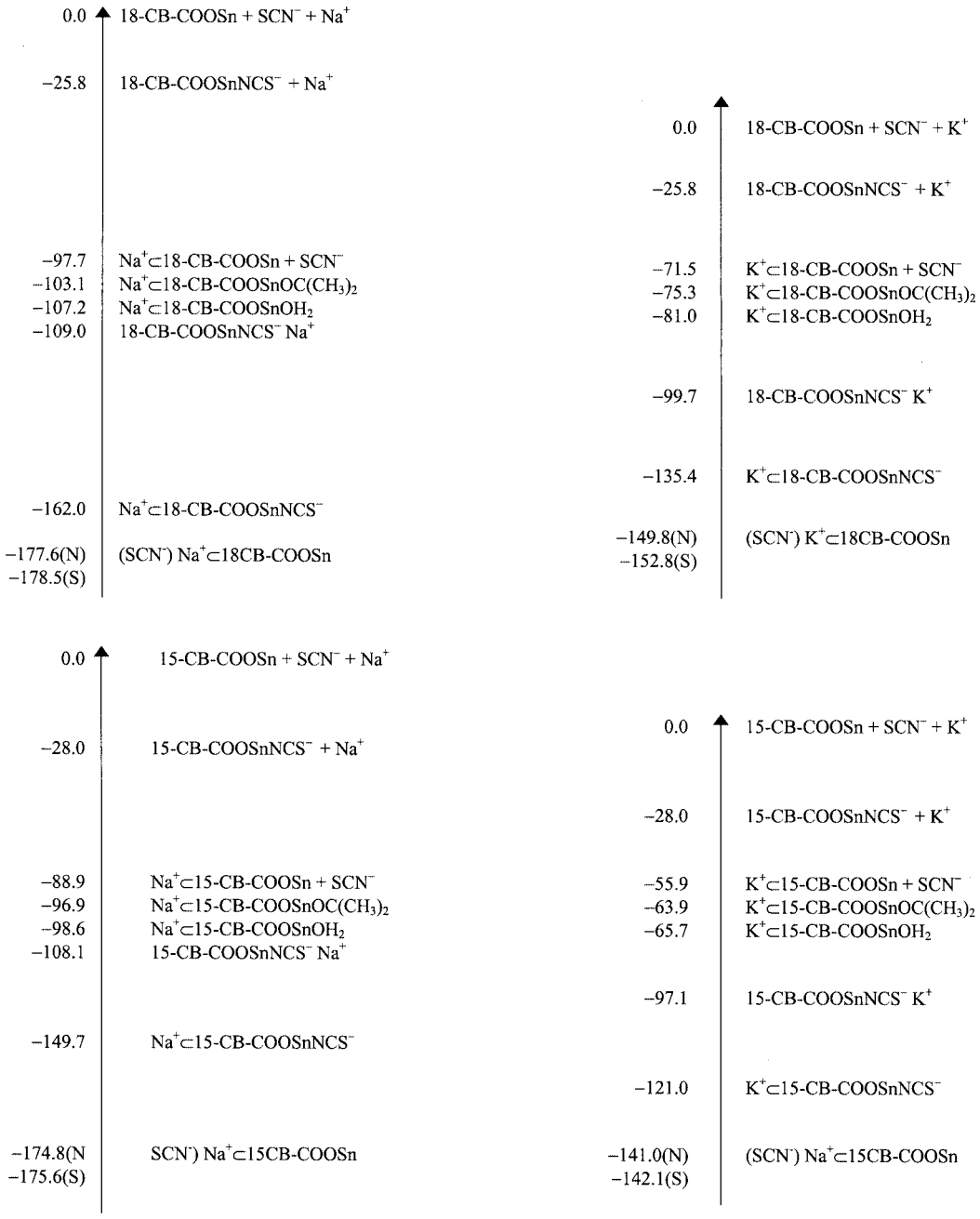



Figure 2. Diagram of stabilisation energies (B3LYP level) for (top left) the [18]crown ether complexes with different nucleophiles and $Na^+$, (top right) the [18]crown ether complexes with different nucleophiles and $K^+$, (bottom left) the [15]crown ether complexes with different nucleophiles and $Na^+$, and (bottom right) the [15]crown ether complexes with different nucleophiles and $K^+$; the methyl groups on tin are omitted for clarity

$C_6H_3COOSn(CH_3)_3$, nucleophiles either charged or uncharged and of variable softness ($SCN^-$, acetone and $H_2O$), and cations ($Na^+$ and $K^+$) are shown in Figures 2a−d. The hardness sequence of the above nucleophiles was calculated at the level outlined in the previous section to yield: $H_2O$ (8.42 eV) > acetone (5.91 eV) > $SCN^-$ (4.36 eV). The investigated complexes displayed interactions between a nucleophile and the tin atom on one hand, and on the other hand between the alkali cations and either the crown ether cavity or the nucleophilic sulfur atom of the $SCN^-$ anion.

The stabilisation energies for the complexation of the crown ether tin derivative with $SCN^-$, $H_2O$ and acetone were calculated both with $Na^+$ and with $K^+$ in the crown ether moiety of the molecule. Initially the nucleophiles were positioned at a distance of 2.20 Å from the tin atom and forming an angle of 180° between the attacking atom of the nucleophile (the oxygen atom for water or acetone and the N atom for $SCN^-$), the tin atom and the oxygen atom of the carboxylate group bound to tin. The final geometry of the complex of acetone and water with Sn was almost ident-

ical for both crown ether tin derivatives, the final distance between the Sn atom and the attacking nucleophilic atom in all cases being between 2.55 and 2.56 Å. The deviations with respect to the original NSnO(7) angle in the X-ray data were only 3.2° and 3.5° for both crown ethers. For the complex with $SCN^-$, the final distance between the Sn atom and the attacking N atom was 2.10 Å and the deviation in the angle was 3.0°.

This orientation (attacking N and not S) was considered first in view of the crystallographic data,[9] this regioselectivity being further discussed below.

The much smaller Sn−N distances of 2.10 Å − in comparison with the Sn−O distance of 2.55 Å − in the water and acetone complexes suggest a stronger complex (vide infra).

The results of the calculations of the stabilisation energies obtained as a result of the interaction of the $SCN^-$, $H_2O$ and acetone nucleophiles with the tin atom and the $Na^+$ or $K^+$ cations with the crown ether moiety are shown in Figure 2a−d.

The influence of the nature of the cation and the crown ether size is discussed first on the basis of MEP calculations. The MEP contours of the crown ethers (see Figures 3 and 4) show that the crown cavity is associated with negative values of the electrostatic potential while the regions outside the crown ether ring are associated with positive values of the electrostatic potential. This behaviour of the MEP thus straightforwardly explains the positions of the $Na^+$ and $K^+$ cations in the crown ether cavity.

In order to find where the minimum (expected to appear in a region with a substantial accumulation of electronic density) was located, we calculated the potential on a straight line over a distance of 10 Å from 5 Å above to 5 Å below the averaged crown ether plane. The results of this calculation can be seen in Figure 5; the minimum was found exactly at the point where the cation should be located and, moreover, a more negative value is associated with the [18]crown-6 ether (−0.1452 a.u.) than for the [15]crown-5 ether (−0.1062 a.u.).

$Na^+$ complexes are systematically more stable than $K^+$ complexes, which can be correlated with the larger ionic radius of $K^+$ (133 pm versus 68 pm for $Na^+$) taking into account the space available in the crown ether.[46] It is also in accordance with the greater hardness of $Na^+$ than of $K^+$, thus interacting more favourably with the hard environment constituted by the ring oxygen atoms of the crown ether moieties. These observations are confirmed by the stabilisation energies calculated for the [18]crown-6 with $Na^+$ (97.7 kcal·mol$^{-1}$) and with $K^+$ (71.5 kcal·mol$^{-1}$) and for the [15]crown-5 ether, for which the stabilisation energy with $Na^+$ is 88.9 kcal·mol$^{-1}$ and with $K^+$ 55.9 kcal·mol$^{-1}$ (see Figure 2). As can be observed, higher stabilisation energies are observed for both cations with the [18]crown ether than with the [15]crown.

The interaction with the cation turns out to be more stabilizing than the interaction with the nucleophile. Note, however, that the interaction energies of $SCN^-$-containing complexes are not additive, with deviations of 38.5 and 38.9

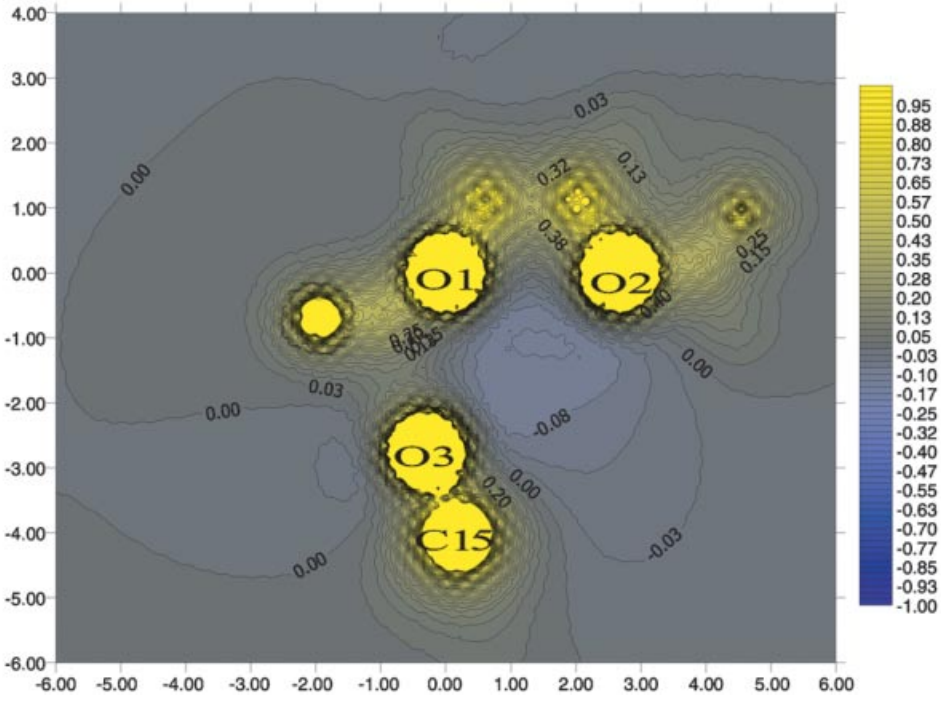



Figure 3. The MEP for the plane containing three of the six oxygen atoms (O1, O2, O3) in the crown ether moiety in [18]crown-6-$C_6H_3COOSn(CH_3)_3$

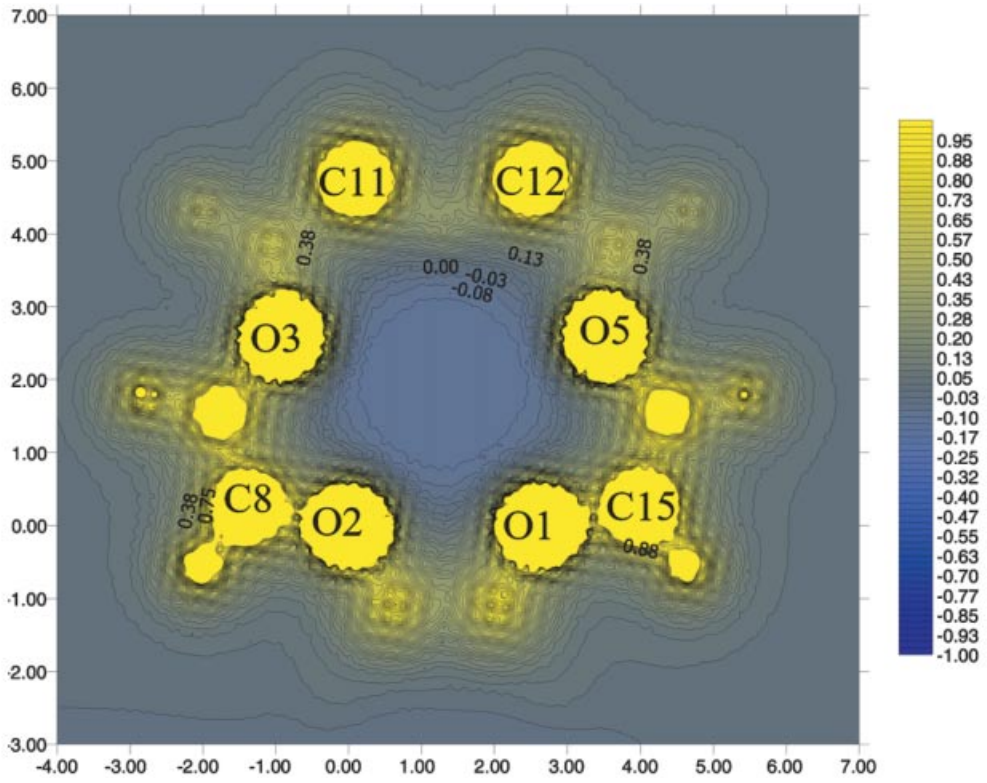



Figure 4. The MEP for the plane containing three of the five oxygen atoms (O1, O2, O3) in the crown ether moiety [15]crown-5-$C_6H_3COOSn(CH_3)_3$

kcal·mol$^{-1}$ for the [18]crown ether with $Na^+$ and $K^+$, respectively, and 32.4 and 37.2 for the [15]crown ether with $Na^+$ and $K^+$, respectively.

One may note that the complexes formed between the tin atom of the crown benzocarboxylate moiety and $SCN^-$ are always more stable (i.e., display more negative values) than for water and acetone both for the $Na^+$ and for the $K^+$ cations, and also both for the [15]crown and for the [18]crown ethers. At first glance, this sequence is in line with the softness sequence $SCN^- >$ acetone $> H_2O$, suggesting that the Sn acts as a soft centre (soft Lewis acid).

In the case of the interaction with $SCN^-$, however, a problem is posed by the regioselectivity. It is known from previous detailed studies on the Fukui function,[47−49] by the present authors among others, that the S atom is the soft centre. It was indeed shown that the sulfur atom in $SCN^-$ was softer than the nitrogen atom, the values being 0.667 a.u. for the condensed Fukui function $f^-_S$ as compared to 0.342 a.u. for the $f^-_N$ (obtained at the QCISD/aug-cc-pVDZ level by use of Bader's population analysis[50]). These values show the same trend as the values calculated in this work (see Table 1).

Table 1 shows that this result is in fair agreement with our calculations, the sequence of local softness values being $s^-_S(SCN^-) > s^-_O(H_2O) \approx s^-_O(\text{acetone}) > s^-_N(SCN^-)$.

This result is a first indication that the Sn atom in the compounds under consideration behaves as a hard atom, since it preferentially interacts with the harder part of $SCN^-$. Note that the charge on the tin atom in both compounds is of the order of +1 a.u. (1.001 a.u. for the [18]crown ether and 1.002 a.u. for the [15]crown ether). This relatively high charge may be due to the structure of the crown ether, where the pentacoordination of Sn, resulting in an almost ideal trigonal-bipyramidal structure[9] in which the two electronegative ligands (the carboxylate group and the nitrogen atom of $SCN^-$) occupy the two apical positions, gives rise to longer bonds with little s character and hence a higher ionic contribution.

The reason that $SCN^-$ as a whole interacts more strongly than acetone or water can then again be traced back to interaction between the Sn moiety and nucleophiles in which charge control (i.e., hard−hard interactions; $SCN^-$ carries a negative charge) dominate. It is found that, in the absence of a net negative charge on the molecule, the oxygen atoms in $H_2O$ and acetone have net charges of 0.72 and 0.40, respectively, making these atoms hard, the sequence being in line with the interaction strength $H_2O >$ acetone. Here we took the net atomic charge as a first indicator of local hardness (see ref.[51] for an in-depth discussion of the problem of finding a well-suited counterpart to local softness).

The hardness of the tin atom has been a point of controversy. From the position of the atom in the Periodic Table, one could conclude that Sn should be relatively soft; indeed, a low value of 3.05 eV is found for the absolute hardness for the isolated atom.[18] In our previous study[36] on the nanocluster $[(RSn)_{12}O_{14}(OH)_6]^{2+}$ (R = $CH_3$), however, we found a local softness value of 0.0074, of the same order as

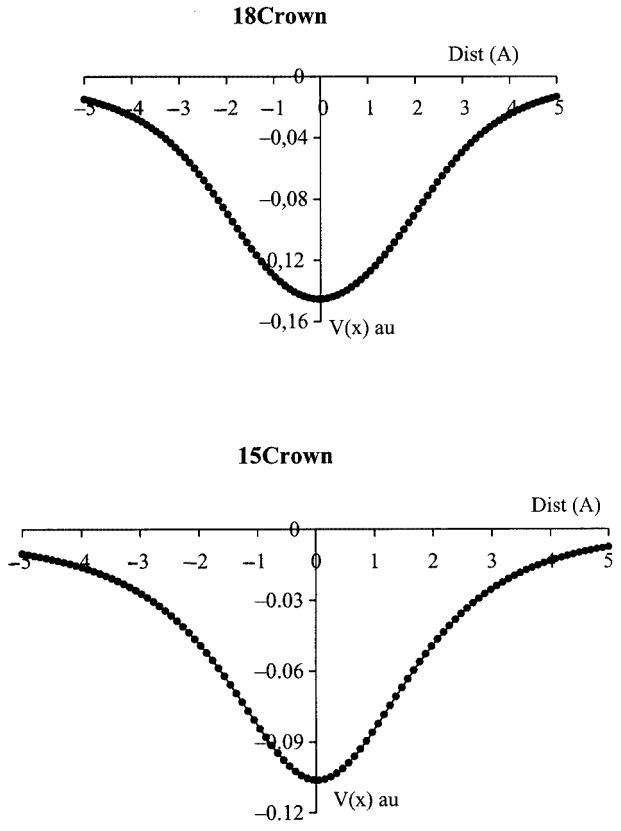



Figure 5. The MEP $V(x)$ (a.u.) for [18]crown-6-$C_6H_3COOSn(CH_3)_3$ and [15]crown-5-$C_6H_3COOSn(CH_3)_3$ along a straight line starting at 5 Å perpendicular to the plane containing the oxygen atoms used in the calculation of the MEP contours (Figures 3 and 4), the intersection point being the $Na^+$ or $K^+$ cation position, in steps of 0.01 Å

the value found here (0.0076), indicating in both cases that the oxophilicity of the tin atom makes it a hard centre, preferring to interact with hard molecules. In addition, the well-known tendency of the tin atom to involve intra- and intermolecularly bridging fluorine atoms is in line with the hardness of Sn in tin fluorides.[52]

Confirmation of a preference for N−Sn interaction over S−Sn interaction was found when the possibility of complexation through the S atom of $SCN^-$ was explicitly studied. In these cases the sulfur atom was placed at the same position as the N atom in the other complexes. Geometry optimisation starting from this alternative complexation mode, however, never provided stable complexes. Moreover, complexes of Sn with $SCN^-$ through the N atom have also been reported elsewhere.[53]

We also calculated complexes in which the nucleophile interacted with the tin atom and the $Na^+$ or $K^+$ were infinitely remote. For the [18]crown-6 we found that the stabilisation energy is 25.8 kcal·mol$^{-1}$ and for the [15]crown-5 28.0 kcal·mol$^{-1}$. By comparison with the data above, it appears that the cation alone in the crown ether hole stabilises the molecule more than when only the nucleophiles are interacting with the tin atom. This can be explained by considering that the crown ether moiety is harder than the Sn atom region. A numerical confirmation (e.g., through the MEP) is quite difficult though, as one region is nucleophilic whereas the other part is electrophilic in nature.

We also studied cases in which $SCN^-$ is bound to the tin atom through the N atom, and the sodium and potassium ions are bound to the S atom of $SCN^-$ (the initial distance between the S atom of $SCN^-$ and the sodium and potassium cations being 2.35 and 2.71 Å, respectively). The energies show the same trends as already obtained in the previous calculations, according to which the [18]crown-6 complex was more stable than the [15]crown-5. They are all less stable than when the cation is trapped in the crown ether cavity. As may be expected in view of the very soft nature of the S centre of $SCN^-$, hard cations interact preferentially with the hard, oxygen-rich crown ether hole.

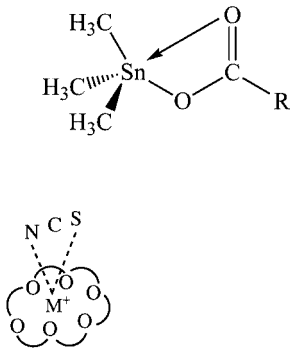
A final set of complexes for the two kinds of trimethyltin crown ether benzocarboxylates was also assessed. In these new cases, $SCN^-$ is directly interacting with the $Na^+$ or $K^+$ ions located in the crown ether hole. For these calculations, both possibilities − that the ions could interact with the N or with the S atom of $SCN^-$ − were considered. The $SCN^-$ was placed at a distance of 2.2 Å from the cation, forming an angle of 90° with the cation and oxygen atoms 1 and 2 (see Figure 1). This geometry was used for both tin ether moieties. For each of the two crown ethers and the two cations, the geometry optimisation was started with a binding situation in which the cation was exclusively interacting either with the nitrogen atom or with the sulfur atom. The optimised end geometries appeared to be roughly identical, since, when starting from the $N^-Na^+$ interaction in the [18]crown ether, optimised $N^-−Na^+$ and $S^-−Na^+$ distances of 2.30 and 4.64 Å were obtained, while when starting from the $S^-Na^+$ interaction fairly similar optimised distances of 2.33 and 4.21 Å, with very close interaction energies of −177.6 and −178.5 kcal·mol$^{-1}$ respectively, were

Table 1. Calculated hardnesses η [eV], softnesses $S$ [eV$^{-1}$], condensed Fukui functions $f^+$ and $f^-$ (atomic units, a.u.) and local softness values $s^+$ and $s^-$ (a.u. eV$^{-1}$); atoms to which condensed functions refer are given in parentheses

| Molecule | η | S | $f^+$ | $f^-$ | $s^+$ | $s^-$ |
|---|---|---|---|---|---|---|
| [18]Crown-6 | 4.07 | 0.246 | 0.0316 (Sn) | | 0.00776 (Sn) | |
| [15]Crown-5 | 4.04 | 0.248 | 0.0309 (Sn) | | 0.00765 (Sn) | |
| $SCN^-$ | 4.36 | 0.229 | | 0.264 (N) | | 0.0299 (N) |
| | | | | 0.620 (S) | | 0.1420 (S) |
| Acetone | 5.91 | 0.169 | | 0.365 (O) | | 0.0619 (O) |
| $H_2O$ | 8.42 | 0.119 | | 0.662 (O) | | 0.0786 (O) |

calculated. Similar calculations for the [18]crown $K^+$ complex give 2.71 and 4.56 Å when starting from $N^-K^+$ and 2.96 and 3.34 Å when starting from $S^-K^+$, with interaction energies of −149.8 and −152.2 kcal·mol$^{-1}$, respectively. For the [15]crown ether, optimised $N^-Na^+$ and $S^-Na^+$ distances of 2.28 and 4.14 Å were obtained, while when starting from the $S^-Na^+$ interaction, optimised distances of 2.75 and 3.54 Å, with very close interaction energies of −174.8 and −175.6 kcal·mol$^{-1}$, respectively, were calculated. Similar calculations for the [15]crown $K^+$ complex give 2.75 and 3.54 Å when starting from $N^-K^+$, and 2.95 and 3.28 Å when starting from $S^-K^+$, with interaction energies of −141.0 and −142.1 kcal·mol$^{-1}$, respectively. These final geometries show very clearly that wherever the N atom of $SCN^-$ is initially located, the final structure always has the nitrogen atom closer to the cation, although with the nitrogen and sulfur atoms arranged in such a way that a bidentate chelation mode with the cation results.

The final geometries of these complexes always yield a pentacoordinate tin atom, since the carboxylate ligands also bind to Sn in a bidentate mode, the oxygen atom of the carbonyl group expanding its coordination (see Scheme 1).




Scheme 1. Bidentate chelating mode of the carboxylate ligand in triorganotin carboxylates, and of $SCN^-$ with the cation positioned in the crown ether

These complexes are more stable (see values above) than the complexes reported in Figure 2. This stability can be attributed to the simultaneous presence of a chelating bidentate mode of the nucleophiles at the levels of both the tin atom and the alkali cation.

Overall, these results fit remarkably well with previous experimental findings from multinuclear NMR studies[9] from which a mixture of several species was proposed to exist in dynamic equilibrium in acetone solution (Figure 6). No direct evidence for species b and c could be given in the NMR study. In the current ab initio study, the species actually merge into a single one with a bidentate mode for $NCS^-$ with the alkali cation. The reason for the lack of NMR evidence lies in the poor sensitivity of $^{23}$Na chemical shifts to coordination changes, the chemical shift difference between completely free $Na^+$ and $Na^+$ interacting with six oxygen atoms amounting to only ca. 10 ppm. A supplementary interaction with external $SCN^-$ is therefore hardly able also to influence the $^{23}$Na chemical shifts. In the crystalline state, the only species observed is the one with the cation trapped in the crown ether cavity and the anion bound to Sn (i.e., of the species calculated here, the most stable one; after $M^+\subset CBCOOSnNCS^-$, species a). In solution, this coexists with the third most stable species, the one where the cation interacts with the sulfur atom of the anion, itself bound to Sn through the nitrogen atom ($CBCOOSnNCS^-M^+$). In addition, $^{117}$Sn NMR chemical shift data reveal that the tin−nitrogen interaction is broken up with increasing temperature, favouring a species in which acetone from the solvent is complexing Sn [$M^+\subset CBCOOSnOC(CH_3)_2$].

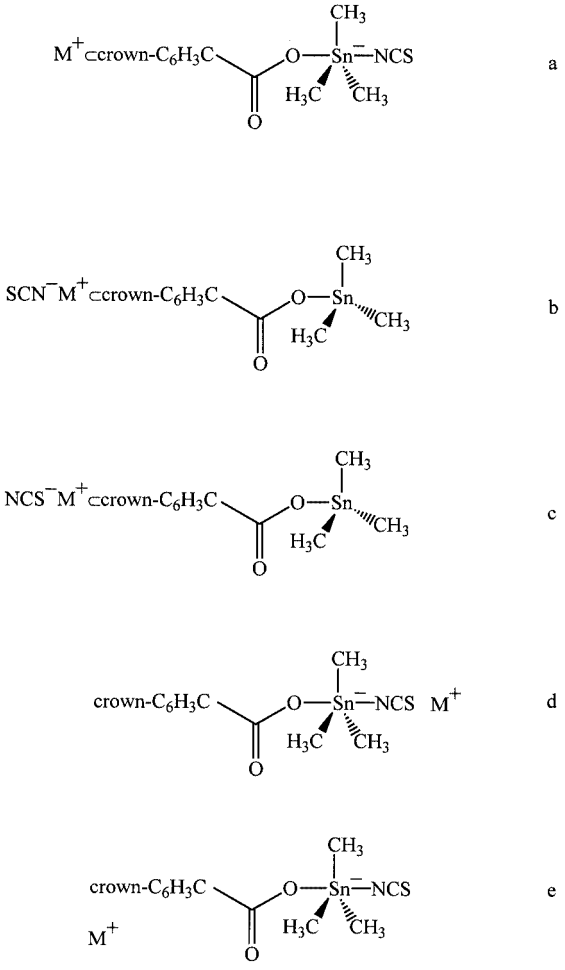



Figure 6. Possible zwitterionic ion pairings

Finally, $^{23}$Na NMR spectroscopic data show the existence of an equilibrium between free $Na^+$ and $Na^+$ trapped in the crown ether hole, this equilibrium favouring $Na^+$ trapping much more for the [18]crown ether than for the [15]crown ether, in line with the results of our calculations indicating more stable alkali cation complexation with the former crown ether than with the latter. Interestingly, when the cation interacts with the sulfur atom of the thiocyanate anion complexing Sn through the nitrogen atom or does not interact at all, the stabilisation energy of the complexes are essentially independent of the crown ether sizes, as they actually should be.

These experiments are also in line with the electrostatic attraction between the positive charge of the cation and the negative values of the MEP being more pronounced for the [18]- than for the [15]crown ether ring (see Figure 5).

## 4. Conclusion

In conclusion, this paper clearly demonstrates that the sites of interactions of the trimethyltin derivatives of [18]crown-6 and [15]crown-5 benzo-4-carboxylates can be predicted by use of DFT-based reactivity descriptors such as the hardness, softness and Fukui function, as well as MEP calculations. The agreement with experimental results is good to excellent, so such calculations both help in interpreting experimental data as well as providing a firm theoretical basis for the different cases of complexation observed.

The HSAB principle, characterising the reactive sites on the basis of local softness, and the Fukui function provide a firm explanation for the reactivity of the tin atom of the crown ether benzocarboxylate towards $SCN^-$, acetone and water. The HSAB concept was also successfully used to explain the preferences of the tin atoms in both crown ethers for binding with the nitrogen atom of $SCN^-$ rather than with the sulfur atom.

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