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A novel field of ab initio studies: complexation of simple anions within neutral cryptands

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Abstract

We present here an ab initio study on anion guest—macrocycle host relationships. The complexation of different simple inorganic anions (F^-, Cl^-, BF_4^- and ClO_4^-) with the neutral cryptand, the macrotricycle $(H_3BN)_4[(CH_2)_n]_6$, ($n=3$–6), has been studied using ab initio Hartree–Fock calculations and density functional theory using the B3LYP hybrid functional. As the side-lengths of the pure cryptands increase with the oligomeric sidechain (n), the cryptand cavity increases as n^3. F^- is the most strongly preferred anion for all cryptands, only for the largest host cavity ($n=6$) complexes are formed exothermally for all anion guests. Morokuma–Kitaura decomposition has been performed to analyse the total interaction energies within the created supermolecules in physically relevant terms including the importance of treatment of the basis set superposition error. According to this scheme the polarisation/charge transfer parts differ in importance amongst the complexes in facilitating a strong binding of the anion guests, but the dominant balance being that of Coulombic attraction and Pauli repulsion.

Keywords: Anion; Cryptand; Supramolecular; Ab initio

1. Introduction

Coordination chemistry has traditionally been fixated on the use of cation cores, i.e. metal ions. Cation coordination and recognition is a very mature area within chemistry, e.g. the advent of cation coordinating macrocycles in the late 1960's [1]. This stands in clear contrast to anion coordination chemistry, which only during the last two decades has evolved as a field and become established, mainly due to interest in biochemical reactions and the need for more efficient catalysts [1–3].

Many of the concepts used in cation coordination chemistry can be transferred to the field of anion coordination. Design of anion coordinating, especially encapsulating, molecular hosts is, however, more problematic than the design of hosts for cations. This is due to the inherent problems in binding anions: in the absence of covalent bonds ion-dipole forces dominate attraction between species, and anions larger than their isoelectronic cation counterparts have lower charge/radius ratios. Thus electrostatic binding is less efficient.

Nevertheless there are also advantages: many simple polyatomic anions have defined geometric shapes (tetrahedrons, octahedrons etc.) and complementary design of host molecules to exploit the extra sensitivity by means of molecular orbital symmetry, softness, size, electron density, and charge–charge distances, etc. can therefore be made. For specific anionic guest species the covalent connectivity within the host molecule can be optimised by precise synthesis—a true target aimed procedure, even if such template-assisted synthesis hitherto is scarce [4].

Crown ethers for cation coordination are based on connecting several Lewis basic groups on a cyclic covalent framework. With the topology constraint increasing (monodentate ligands < linear polydentate ligands < macrocycles < cryptands) the affinity also increases, i.e. chelate effect < macrocyclic effect < cryptate effect, as long as no

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exceptional strain is introduced in the host molecule and no problems with host-guest complementarity results. For this reason macrocycles like crown ethers can, if chosen carefully, bind even the largest alkali cations. An extension is then to use polycycles (cryptands) to obtain even stronger complexes by the virtue of the three-dimensional encapsulation and possibly additional Lewis bases within the ring system, leading to very slow exchange rates.

The analogous strategy for anion binding species would be to use Lewis acidic groups on a similar covalent framework, while taking into account the larger radii of anionic species. To emphasise the relationship with the corresponding cation binding strategy this approach to anion coordinating supramolecular chemistry has been named 'anti-crown chemistry' [2,5].

Various ways to such host molecules has been explored, here we will focus on a specific neutral host molecule that bind the anion of choice via ion-dipole interactions. As Cram noted [6], a rigid host molecule with complementarity to the guest in the way the dipoles are arranged should show the strongest binding (a concept comparable to the cryptate effect)—a demand that is most easily met by arranging them on a polycyclic framework. Thus, host synthesis cannot be made for a large variation of guests, but rather be made by choice of target anion first.

Worm et al. were the first to outline, synthesise, and prove the possibility of using a neutral cryptand and anion-dipole interactions as the means to obtain anion-cryptand complexes. This was done elegantly by reacting a macrotricyclic quaternary ammonium molecule: $N_4[(CH_2)_6]_6$, with $BH_{3(THF)}$, resulting in the neutral cryptand: $(H_3BN)_4[(CH_2)_6]_6$ with dipolar B–N bonds oriented in a tetrahedral arrangement, which make for the possibility to encapsulate anions in a preferential manner [7]. The concept utilizes a rather firm orientation of the dipoles by the high connectivity framework. Henceforth, we will use the expressions macrotricycle and cryptand interchangeably for this and similar compounds.

The knowledge of these types of host compounds can be expanded by quantum mechanical (QM) computational studies on the $(H_3BN)_4[(CH_2)_n]_6$, ($n=3$–6), system (Fig. 1). Our aim with this ab initio study is mainly three-fold: (i) to study the anion encapsulation properties, (ii) to interpret the interaction energies within the created supermolecules in chemically and physically relevant terms, and (iii) to reveal

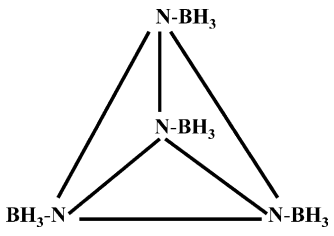

Fig. 1. Schematic figure of the $(H_3BN)_4[(CH_2)_n]_6$ ($n=3$–6) cryptands. Edges $=[(CH_2)_n]$.

the possibilities of using the anion-host complexation to obtain 'free' cations, which can be technologically interesting in e.g. electrolytes and cationic olefin polymerisation catalysts. The former area has been explored using both small boron and nitrogen based anion receptors as additives [8] and by using integrated boron based anion receptors on a polymeric network for polymeric electrolytes [9,10]. The latter work also reported ab initio calculations of the anion to receptor interaction strength.

To the best of our knowledge this is the first work employing ab initio methods on these types of compounds and their complexes, apart from our own recent short paper [11]. Indeed, very few ab initio studies on anion encapsulation within neutral hosts are hitherto reported. Recent relevant studies are for instance the ab initio Hartree–Fock (HF) and density functional theory (DFT) study on the complexation of F^-, Cl^- and Br^- by a tribora-macrocycle by Aldridge et al. [12] and the ab initio works, mainly on polyoxometalates, summarized in the review by Rohmer et al. [13]. The latter mainly uses the molecular electrostatic potential (MEP) as a tool to explore the preferred coordination, while the former includes a small charge transfer (CT) analysis together with the interaction energies having similar interacting groups as the present study. The binding of F^- by the most heavily fluorinated macrocycle in [12] is very strong, reporting binding energies up to $\sim$600 kJ mol^{-1}. A review on computational studies of anion binding receptors can be found in Chapter 9 in Ref. [3]. Most previous work has concerned positively charged compounds or compounds using hydrogen-bonding as the mean to coordinate the anion of choice. For such systems many excellent experimental studies exists e.g. ^{19}F NMR and XRD studies on F^- binding in an aza-ether cryptand [14] as well as a few computational studies e.g. HF and DFT calculations on halide anions in calix [4] pyrrole [15]. For a somewhat similar specie as in the present study, a macrocyclic borane with sp^2 hybridised B atoms connected the same way as the H_3BN groups, a computational study on semi-empirical level revealed successful encapsulation of four different monoatomic anions [16]. In 1995 Sohlberg and Tarbet reported semi-empirical INDO1 calculations on (amongst others) the $(H_3BN)_4[(CH_2)_6]_6$ system with the halide series of ions F^-, Cl^- and Br^- as guest atoms [17]. They obtained qualitative agreement with the experimentally preferred binding reported in [7].

Unfortunately, the use of semi-empirical methods, even if probably the most appropriate at the time for computational reasons, can lead to false conclusions due to inherent weaknesses. The accuracy is generally lower than for ab initio methods and is also highly dependent on the types on interactions and elements being modelled—such variations are less pronounced in ab initio methods. Especially, the semi-empirical parameters used have not been optimised for the interactions present in these types of compounds, since reliable experimental data is virtually non-existent. Also non-uniform and un-predictable errors

are more often found in semi-empirical calculations [18]. The qualitative success of the INDO1 and AM1 calculations should be seen in the light of the guests having the same charge (in [16] also O^{2-} was used), shape and type of electron configuration (all having s^2p^6 valence shell). Additionally, the interaction strengths obtained from semi-empirical studies are difficult to give an unambiguous interpretation that is physically tenable.

As for ab initio studies these are in general more reliable and it is rather straightforward to perform analysis of the interaction energies with respect to e.g. Pauli repulsion, Coulombic attraction, polarisation, and CT. To further strengthen the ab initio approach to determine the strengths of the interactions DFT methods using the B3LYP functional are added to the basic HF level calculation, revealing the importance of electron correlation. The effect of different basis set sizes is also to be considered, as often deemed especially important when dealing with electron-rich systems. As for the atomic models, the present study not only varies the size of the hosts, but also the elemental and molecular electron configurations of the guests. All guest anions have a single negative charge, but intra-molecular charge distribution is present for BF_4^- and ClO_4^-. In the end, the range of possible interactions and the computational methods applied will hopefully together help us to obtain data allowing a matching of hosts and guests to be recommended, maximizing the host-guest interaction.

Molecular mechanics, HF, and hybrid DFT calculations have been performed for the $(H_3BN)_4[(CH_2)_n]_6$, ($n=3$–6) system, with and without anions (F^-, Cl^-, BF_4^-, or ClO_4^-) inserted.

2. Computational details

To ascertain that the study is not seriously affected by starting geometries built in any unjustified manner the conformational space of all the hosts was explored using molecular mechanics (MM) calculations prior to any QM calculations. To systematically explore the conformational space rapidly becomes insurmountable even for medium sized molecular systems. Thus, with a relevant resolution in the dihedral angle variation, a truly systematic approach is not computationally justifiable for the present systems, even at MM level, and we, therefore, apply a Monte–Carlo (MC) based conformation search using the MMFF force field as implemented in the Spartan'02 program package [19]. The MMFF model has been shown to be quite successful in providing conformations and quantitative estimates of related energy differences [20]. Accordingly, initial conformational searches were performed by a MMFF MC strategy for $(H_3BN)_4[(CH_2)_n]_6$, using different alkane side-lengths ($n=3$–6) and a dihedral resolution of 30°.

The resulting conformers were subject to full geometry optimisations using MMFF, but generated conformers with BH_3-units inside the cryptand cavity were excluded from further analysis. Using the resulting MMFF host structures as templates, the anion guests were inserted and the host-guest combinations geometry re-optimized using MMFF. Subsequently, the unique lowest relative energy structures from each sub-study were transferred to full QM optimisations using HF methods employing the standard 6-31G* basis set (HF/6-31G*). The $n=4$ structures were used as reference compounds to reveal whether the relative energies obtained from the MMFF calculations could be used to pre-screen candidates for the HF level optimisations. From this we concluded that only a few of the lowest energy conformers within each sub-study were needed to be transferred to the HF level for $n=5$ and 6 (saving tremendous amounts of computational resources).

Additionally, to obtain more accurate relative energies as well as binding energies, single-point energy calculations using larger basis sets (HF/6-311+G*//HF/6-31G*), SP1, and electron correlation (B3LYP/6-311+G*//HF/6-31G*), SP2, [21–23], were performed for the most stable host-guest combinations.

The largest cryptand composes 44 heavy atoms and 84 hydrogen atoms (128 atoms in total), which is a standard computational task size with the computational capabilities at hand today. However, as all the structures are very flexible and have flat potential energy landscapes the geometry optimisations were very time-consuming due to the large number of iterations needed; a typical case demanded ~80 optimisation steps at the HF/6-31G* level. Only for the most stable structures for each sub-study analytical second derivatives with respect to nuclear displacements were evaluated to validate the energy minima.

The anion volumes were calculated using a MC integration scheme in GAUSSIAN03 [24] at the HF/6-31G* level and a 0.001 e $bohr^{-3}$ electron density cut-off. As the corresponding calculation is not possible for the cavity, the cavity volumes of the hosts were simply calculated as regular tetrahedral structures with the edges (a) equal to the average N–N distances and accordingly the volume $V=a^3\sqrt{2}/12$. Unfortunately, these different schemes for computing the host cavity and guest anion volumes imply an ambiguity in the correlation of volumes. The program packages Spartan'02 [19] and GAMESS [25] were used for all other calculations.

The binding energies were obtained at each QM computational level as the differences in total electronic energies (ΔE_{el}) between the supermolecules formed and the components separately, in their respective minimum energy geometries. In order to in more depth analyse the anion guest to cryptand host interactions a Morokuma–Kitaura decomposition of the supermolecules was performed as implemented in GAMESS [26]. The interaction energies within the created supermolecules are this way interpretable in physically relevant terms: Pauli repulsion, Coulombic attraction, polarisation, and charge transfer. The basis set super-position error (BSSE) was quantified.

3. Results and discussion

First we report the obtained energies of supermolecule formation. Second selected geometry data for the pure macrotricycles and the supermolecules are presented. Third the resulting binding energies are analysed more rigorously with an energy decomposition scheme. Finally we summarize and suggest the most appropriate guest-host combinations based on the obtained data and discuss the advantages/difficulties with the chosen approach.

3.1. Energies of supermolecule formation

In Fig. 2 the differences in electronic energies upon super-molecule formation are presented for all host-guest combinations and all QM computational levels. Only data for the most stable complex for each combination is shown. In total 8 combinations readily form complexes, 1–3 combinations are borderline cases, and 5–7 combinations are energetically impossible. For the two smallest hosts ($n=3,4$) we find exothermally formed complexes/supermolecules only with the smallest guest anion F^-. All host-guest combinations show increasing exothermal energies with increasing the host size, apart from the combination of $n=6$ and F^-. The reason hereof we will return to later. Only for $n=6$ all guests are accommodated exothermally.

Using the highest computational level energy data the strongest complexes are formed with the $n=4$–6 hosts and F^- and $n=6$ and Cl^-. All computational levels show approximately the same behaviour across all systems. The HF/6-31G* value of -215 kJ mol^{-1} obtained for F^- and $n=3$ is considerably larger, by 23%, than our own previously reported value of -175 kJ mol^{-1}, a study where no thorough conformational search was performed prior to complex optimisation [11], showing the importance of investigating the flexibility of the host for a correct energy of encapsulation.

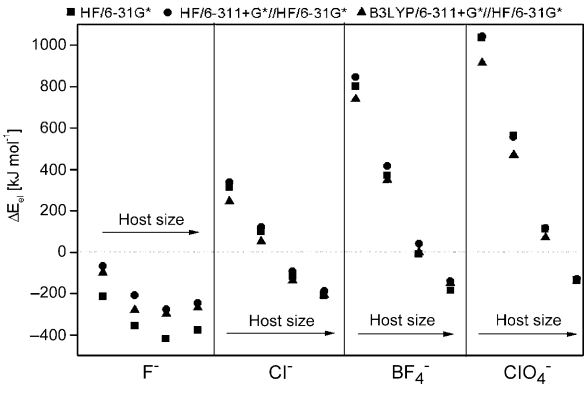

Fig. 2. Energies of super-molecule formation for each anion host and guest combination at three different computational levels. The binding energies (ΔE_{el}) were obtained as the differences in total electronic energies between the supermolecules formed and the components separately, in their respective minimum energy geometries.

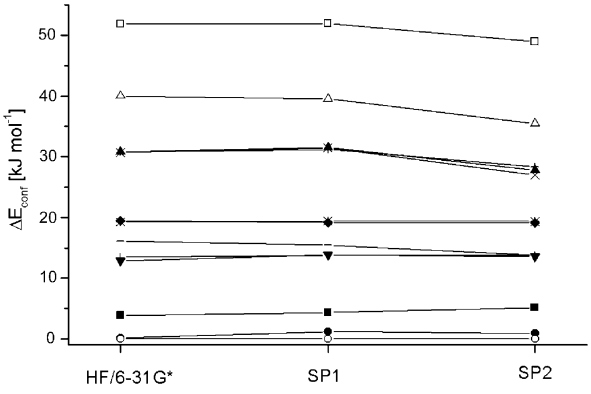

Fig. 3. The relative energies of $n=4$ conformers using different computational methods.

To further examine the role of the conformational search and our range of conformers exported to the QM level the relative energies, ΔE_{conf}, for the obtained $n=4$ conformers, 13 unique, are shown in Fig. 3. The maximum energy difference is almost constant across the three QM computational levels: 52, 52, and 49 kJ mol^{-1}, respectively. The 6 lowest energy conformers are within 16, 15, and 14 kJ mol^{-1}. For $n=3$ and the resulting lowest 6 unique conformers the corresponding values are: 16, 17, and 12 kJ mol^{-1}. It is encouraging that the same conformers are energetically favoured for all computational levels (Fig. 3), thus making the export of only a few low energy conformers to the SP calculations for $n=5,6$ a valid simplification. However, this is not necessarily transferable to the host-guest complexes. Therefore, the variation in energies was separately checked for host-guest structures at different levels for $n=3,4$, resulting in a similar behaviour (not shown).

There is experimental data only for the largest host, $n=6$. In Ref. [7] this host was reported by NMR and electro-spray ionisation mass-spectrometry (ESI-MS) methods to be able to easily enclose a chloride or a bromide anion, and by ESI-MS also the inclusion of an iodide anion could be observed. Using simple force-field/MD simulations the authors of Ref. [7] showed that Br^- and CN^- anions could be incorporated ($\Delta H_{form}=-67$ and -109 kJ mol^{-1}, respectively), which however, failed for a BF_4^- anion. Our present energies suggest that also the two largest anions, BF_4^- and ClO_4^-, can be contained within this host, in clear contrast to the results of Worm et al. However, in the present work there is no need for penetration, which can explain the obtained differences. The interaction and the energies will be more thoroughly analyzed using Morokuma–Kitaura decomposition after the summary of structural results with impact on the further discussion.

3.2. Geometry parameters of anions, hosts, and supermolecules

All the $(H_3BN)_4[(CH_2)_n]_6$ macrotricycles studied here have six equal alkyl linkages with the sp^3-hybridised N atoms in the corners of approximate tetrahedrons. In Table 1

Table 1
Selected geometry data for hosts, guests, and supermolecules (Å)

	Guest		*n*			
			3	4	5	6
R(N–N) [a]	None		4.556(6)	5.500(6)	7.004(6)	7.205(6)
	F^-		4.642(6)	5.626(6)	6.568(6)	7.380(6)
	Cl^-		4.822(6)	5.723(6)	6.708(6)	7.621(6)
	BF_4^-		4.908(6)	5.860(6)	6.804(6)	7.934(6)
	ClO_4^-		4.939(6)	5.906(6)	6.888(6)	7.780(6)
R(N–M) [a]	F^-		2.949(4)/2.722(3)	3.454(4)/3.392(3)	4.036(4)/3.952(3)	4.532(4)/4.119(3)
	Cl^-		2.960(4)/2.939(3)	3.551(4)/3.409(3)	4.114(4)/3.973(3)	4.682(4)/4.654(3)
	BF_4^-		3.006(4)	3.612(4)	4.178(4)/4.025(3)	4.863(4)
	ClO_4^-		3.025(4)	3.646(4)	4.226(4)/4.125(3)	4.766(4)
r(N–X) [a]	F^-		2.949(4)/2.722(3)	3.454(4)/3.392(3)	4.036(4)/3.952(3)	4.532(4)/4.119(3)
	Cl^-		2.960(4)/2.939(3)	3.551(4)/3.409(3)	4.114(4)/3.973(3)	4.682(4)/4.654(3)
	BF_4^-		2.858(12)/2.710(4)	3.430(12)/2.893(4)	3.945(12)/3.716(4)	4.595(12)/4.410(4)
	ClO_4^-		2.882(12)/2.773(4)	3.458(12)/2.913(4)	3.992(12)/3.720(4)	4.497(12)/4.349(4)
r(M–X) [a]	BF_4^-	1.394	1.363(4)	1.371(4)	1.381(4)	1.390(4)
	ClO_4^-	1.450	1.421(4)	1.427(4)	1.439(4)	1.448(4)

[a] The number of distances averaged over are given within brackets, M = central atom, X=F or O.

selected geometry data (distances) obtained for the hosts, guests, and the resulting supermolecules are presented. The intra-molecular average distances are presented with total number of distances averaged. For the polyatomic guests we can discriminate between preferences for mono-dentate coordination towards the B–N dipoles or the tri-dentate coordination resulting from directing the M–X bonds towards the geometric centres of the ~triangular (hollow) sides of the tetrahedrons. The r(N–X) measure show small differences for $n=3$ and 6, slightly larger for $n=5$, and a very large difference for $n=4$. A similar behaviour is noted for both MX_4^- anions. Thus for $n=3$ the M–X bonds are directed towards the sides to minimize repulsion and for $n=6$ the distances are long enough not to make for a strong directional dependence. For $n=4$, and to a lesser extent $n=5$, strong interactions are formed via dipoles interacting with one X atom each. These results are not contradicted by the energy results presented; those refer to the respective free species as references.

For the mono-atomic guests the *r*(N–M) measure reveals if the ion is centred or displaced from the middle. Here F^- and Cl^- behave quite differently. The fluoride anion is clearly tri-dentate in the $n=3$ host having bond distances on par with the N–X obtained for the MX_4^- anions. For $n=6$ the reason for tri-dentate coordination probably is a beneficial conformational change of the host resulting in one N–M distance of 5.77 Å. These distances combined with the energies in Fig. 2 support the importance of as many interactions as possible to get maximum interaction strength as $n=6$ shows a weaker coordination strength than $n=4,5$. Cl^- on the other hand is almost 'pushed' towards a central position for the $n=3$ host, then forming three bonds with the preferred bond lengths within the $n=4,5$ hosts, while the $n=6$ host again makes the central position preferred, now resulting in the strongest complex according to Fig. 2. To summarise: the position within the differently sized hosts is dependent on how many interactions that are formed with the four corners of the $(H_3BN)_4[(CH_2)_n]_6$ macrotricycles and if four equally strong interactions are feasible the strongest complexes are obtained.

Does the encapsulation affect the intermolecular geometry of the MX_4^- anions? In general geometry effects on the inter-molecular distances of the polyatomic anions are only discernible when the formation of the supermolecule is endo-thermal and a strong repulsion from the host compresses the guest anions. For the largest host ($n=6$) for which all supermolecules are formed exothermally the distortions of the anion geometries are negligible: 0.004 and 0.002 Å, for BF_4^- and ClO_4^-, respectively.

In Fig. 4 the cavity volume for each system is plotted as a function of *n*, together with the computed volumes for the anion guests. As *r*(N–N) increases almost linearly with *n* the volumes are basically proportional to n^3. There is thus no discernible intra-molecular dipole–dipole repulsion for small values of *n*, nor any size-effects due to the increased side-chain linkage degrees of freedom for large *n*. While

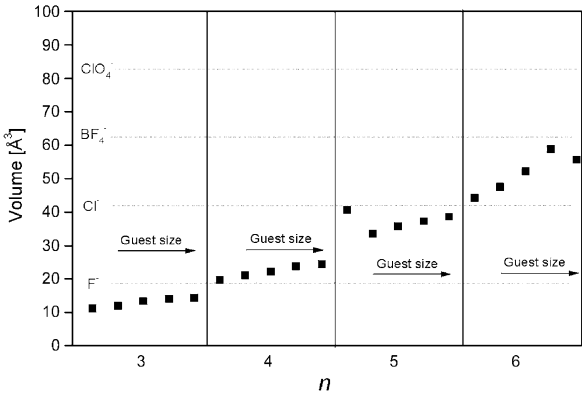

Fig. 4. Volumes for the cryptands with and without guests (first point for each host). Computed volumes for the anions (dotted lines): F^-: 19 Å^3, Cl^-: 42 Å^3, BF_4^-: 62 Å^3, and ClO_4^-: 82 Å^3.

remembering the ambiguity in the methods of computing the volumes of the guests and hosts, in general the cavity-sizes obtained are very small; in most cases smaller than the anions intended to form supermolecules with. However, even the smallest cavity ($\sim$11 Å^3), $n=3$, can enclose an anion exothermally (F^-). The reason hereof was proposed by Jacobson and Pizer: when the guest to host interaction no longer is purely ionic a suitable cavity can be smaller than the pure anion itself [16]. From Fig. 4 we find that even a cavity size less than $\sim$60% of the free anion volume allows exothermal encapsulation, though the shape of the anion guest vs. the host cavity affects this comparison together with the very simple cavity calculation. The anion vs. cavity volume, expressed in the present way, is thus a poor measure for encapsulation capacity, at least for these sizes of anion guests and host compounds.

All anion guests affect the resulting cavity volumes, however, only to a small extent. The expansion of the host with a guest present is almost a general feature. Only upon encapsulation of ClO_4^- within the largest host there is a breaking of the trend 'larger guest—larger supermolecule' (Fig. 4). The empty $n=5$ host has a very special geometry making this comparison less straightforward, but amongst the host-guest complexes the same trend as for $n=3,4,6$ is followed.

3.3. Decomposition of interaction energies within the created supermolecules

By using the Morokuma–Kitaura (MK) scheme as implemented in GAMESS we obtain the results in Table 2. The terms used are explained thoroughly in [26–28]. First we focus on the difference between the interaction energies, E_{int}, and the electronic energy differences, E_{el}, resulting from the conformational/structural relaxation rearrangement of both host and guest upon formation of the supermolecule. This difference is tabulated as $E_{relax}=E_{el}-E_{int}$. As expected this is more important for the smaller hosts, and largest for the endothermally formed supermolecules, while for $n=6$ the size of this structural re-arrangement energy is small compared to the interaction energies.

However, the comparison made inherently compares two different computational situations: one where the basis functions cannot be shared between the host and guest (the separate species in their respective minimum energy structures) and one where they can (the supermolecule calculations). Thus, the effect of BSSE must also be considered and was found to be unexpectedly large for these systems. While the BSSE uncorrected E_{int} show more complexes to be exoergically formed, the BSSE corrected E_{int} show the behaviour we expect from Fig. 2 (apart for the combination $n=4$ and Cl^-).

Turning to the details of the energy contributions, for the smallest host ($n=3$) the Pauli exchange repulsion is larger than the Coulombic, electrostatic, attraction for all guests, increasing rapidly with the guest size, and only the strong charge transfer/polarisation effect on the host of the F^- guest can make a supermolecule beneficial. For the mid-size hosts ($n=4,5$) the guest-host distances become more longer and the Pauli and Coulombic contributions are more in balance, especially for the mono-atomic guests, giving the other terms decisive roles, making the suggestions of Jacobson and Pizer [16] about the role of charge-transfer credible. Finally for $n=6$, the Pauli repulsion is smaller than the electrostatic attraction and, therefore, all host-guest complexes are formed exoergically.

Using the guest specie as the reference tool, Table 2 reveals F^- to strongly affect the host in all complexes by charge transfer and polarisation, with a maximum effect for $n=4$, and then slightly reduced for the larger hosts, probably due to bad orbital overlap for these larger hosts. For Cl^- and BF_4^- the same reduction occurs first for $n=5$–6. In contrast ClO_4^- has an almost constant effect on the host energies. The relative contribution of

Table 2
Decomposition of the interaction energies using the Morokuma–Kitaura scheme including BSSE (kJ mol^{-1})

N	Guest	E_{int}	E_{el}	E_{relax}	E_{int}[a]	E_{ES}	E_{XR}[a]	$E_{CTPLX(guest)}$[a]	$E_{CTPLX(host)}$[a]	E_{RES}[a]
3	F^-	−363	−215	148	−182	−400	408	−26	−275	112
	Cl^-	29	314	285	70	−469	680	−37	−148	43
	BF_4^-	141	801	660	254	−372	743	−51	−141	76
	ClO_4^-	282	1036	754	353	−453	926	−50	−110	42
4	F^-	−400	−357	43	−222	−345	323	−13	−296	109
	Cl^-	−62	98	160	−25	−379	495	−32	−153	44
	BF_4^-	−7	370	377	98	−342	553	−28	−152	67
	ClO_4^-	111	561	450	170	−396	680	−37	−115	38
5	F^-	−427	−420	7	−263	−233	127	33	−261	70
	Cl^-	−154	−117	37	−119	−264	263	−18	−135	35
	BF_4^-	−101	−10	91	−7	−269	370	−8	−156	56
	ClO_4^-	−48	112	160	3	−270	368	−14	−112	31
6	F^-	−393	−378	15	−248	−189	79	45	−236	54
	Cl^-	−199	−210	−11	−169	−168	87	−2	−107	21
	BF_4^-	−206	−186	20	−127	−160	111	21	−133	33
	ClO_4^-	−149	−136	13	−104	−161	126	5	−97	21

[a] incl. BSSE.

the polarisation and the charge transfer to the total interaction, for the exoergically formed supermolecules, varies between $>100\%$ (F^-) and 63% (Cl^- and $n=6$).

Finally, the residual energy from the MK analysis is rather large for the two strongest complex interactions, but for all other complexes it is well within accepted error and far from dominating the analysis. A resort to for example RVS analysis was not deemed useful as weak, non-covalent interactions are probed worse using RVS and RVS gives less information on partial contributions [27].

While the analysis above treats guests, hosts, and supermolecules correctly several important factors are neglected. Examples are: solvent effects, the counter-ion, the need for the anion intrusion into the host via the triangular sides etc. Some type of dynamics calculation (e.g. MD) may handle all these factors, but to assure a correct treatment such calculations must be performed with potentials sensitive to the special interactions.

4. Conclusions

Using QM calculations on MC generated conformers of host-guest complexes have successfully revealed formation of supermolecules with encapsulated anions with these very special cryptands. By calculation of the volumes of the cavities and anion volume we find that, using the present computational strategy, the cavity size cannot be directly used as a probe of encapsulation capacity of the hosts. We find different types of coordinations within the formed supermolecule, while the MK energy decomposition reveal a decisive role of the Coulombic/Pauli balance, with the exception of F^- as host where polarisation/charge transfer contributes significantly. Depending on reference system choices and BSSE the maximum interaction/formation strengths are in the range -427 to $-263\ \mathrm{kJ\ mol^{-1}}$. Comparing the strengths of interaction with those of the respective lithium salts promises possibilities of using these types of cryptands practically—not necessarily to obtain 'anion-free' aprotic electrolytes, but with significantly reduced lithium-ion to anion interactions.

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