

1. Chemistry with Weakly Coordinating Anions – Introduction and Theoretical Background

Many of the cations a preparative chemist sketches on paper when elucidating a novel reaction mechanism have already been observed on experimental grounds, however, not in the condensed phases that synthetic chemists usually work in, but rather in the gas phase inside a mass spectrometer. If not accessible on experimental grounds, these cations (and other species) have been modeled by one of the advanced quantum chemical methods, again formally in the gas phase at 0 Kelvin. One example for such a species was the ^tBu cation $C(CH_3)_3^+$, which is a key to understanding S_N1 -type reactions. Due to the fundamental importance of this cation and through using very weakly basic conditions throughout it was possible to study the isolated ^tBu cation. Initially this was only possible in solution,^[1] but later the first crystal structure appeared^[2] and finally in 2004 a report on "Putting ^tBu cation into a bottle" was published.^[3]

To put a gas phase cation into a bottle in condensed phases the cation must be partnered with a suitable anion. To allow the formation of stable salts of such interesting but very reactive cations, one needs very special anions of low nucleophilicity and basicity on the one hand but of chemical robustness towards electrophiles and oxidizing agents on the other hand. Anions that fulfill these criteria are called Weakly-Coordinating Anions (WCAs), since *non-coordination* can never be achieved in condensed phases. Rather one can exchange a few strongly coordinating interactions for many but very weakly-coordinating interactions. Thus, WCAs allow one to stabilize strongly acidic gas phase species, highly electrophilic metal and non metal cations or weakly-bound Lewis acid-base complexes of metal cations.^[4-8] Examples of this kind of unusual and fundamentally important cations include $Au(Xe)_4^{2+}$,^[9] Xe_2^+ ,^[10] HC_{60}^+ ,^[11] Me_3Si^+ , $Ag(CO)_2^+$,^[12] N_5^+ ,^[13] $Si(Cp^*)^+$ ($Cp^* = C_5(CH_3)_5$),^[14] $P(Cp^*)_2^+$,^[15] $Ir(CO)_6^{3+}$ ^[16] and many more. Apart from being very useful in fundamental chemistry, WCAs

have a very strong standing in applied chemistry. For instance, WCAs are important for homogenous catalysis,^[17, 18] polymerizations,^[8, 19] electrochemistry,^[20] ionic liquids,^[21] photolithography,^[22] lithium ion batteries or super capacitors.^[23] However, no WCA fulfills all demands, but one has to choose a suitable anion according to a balance of steric and electronic interactions of the cation and the anion as well as anion stability considerations.

Accordingly, a variety of different WCAs has been introduced; especially throughout the last two decades. Starting from the classical BF_4^- and MF_6^- anions, a frequently used approach to synthesize new WCAs is to attach large sterically demanding fluorinated alkyl or aryl groups to a Lewis acidic central atom. Thus, WCAs tend to be relatively bulky anions in which the negative charge is dispersed over a large surface area. Another approach which is almost as frequently used as the first one uses (pseudo)halides to link two (or more) Lewis acids which leads to even bulkier anions with more than one Lewis acidic center.

This technique leads to fluorometallates of the type $[\text{M}_n\text{F}_{5n+1}]^-$ ($\text{M} = \text{As}, n = 2; \text{Sb}, n = 2-4$) (Figure 1).

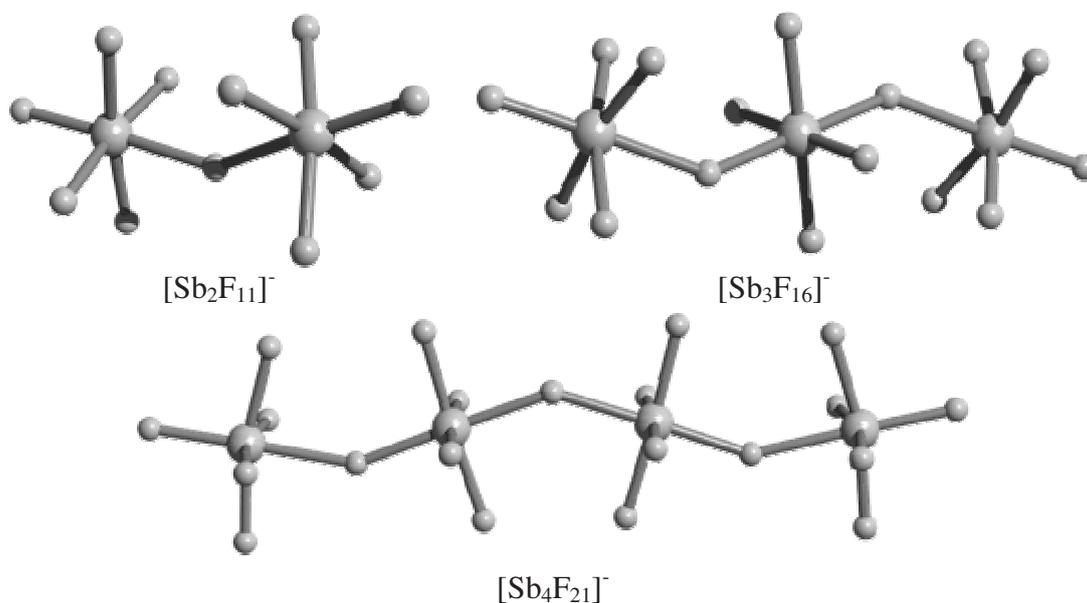


Figure 1. Structures of the multinuclear fluorometallate based $[\text{Sb}_2\text{F}_{11}]^-$ (top left) $[\text{Sb}_3\text{F}_{16}]^-$ (top right) and $[\text{Sb}_4\text{F}_{21}]^-$ (bottom) as ball and stick models.

Anions of this type are very robust against decomposition, but they can only be handled in especially designed fluorine laboratories. Further more, in solution $M_nF_{5n+1}^-$ does only occur as mixtures with varying values of $n = 1-4$, which makes crystallization more difficult and provides the free Lewis acid MF_5 that may also serve as an oxidizing agent and thus may lead to unwanted side reactions.

Substitution of fluorine in BF_4^- is an illustrative example for the first approach and leads to polyfluorinated tetraaryl- or tetraalkylborates $[B(R^F)_4]^-$ ($R^F = CF_3$,^[24, 25] C_6F_5 ,^[26] $C_6H_3(CF_3)_2$,^[27] and others), a class of anions nowadays mainly used in homogenous catalysis (Figure 2). Salts of the last two anions are commercially available and thus promote their use in many applications. Combination of both synthetic approaches, i.e. reaction of two equivalents of $B(C_6F_5)_3$ or a related Lewis acid with a strong and hard nucleophile X^- such as CN^- or NH_2^- leads to dimeric borates $[X(B(C_6F_5)_3)_2]^-$ ($X = CN$,^[7, 28] NH_2 ^[29] and others). These dimeric borates are simple to prepare and surprisingly stable (Figure 2).

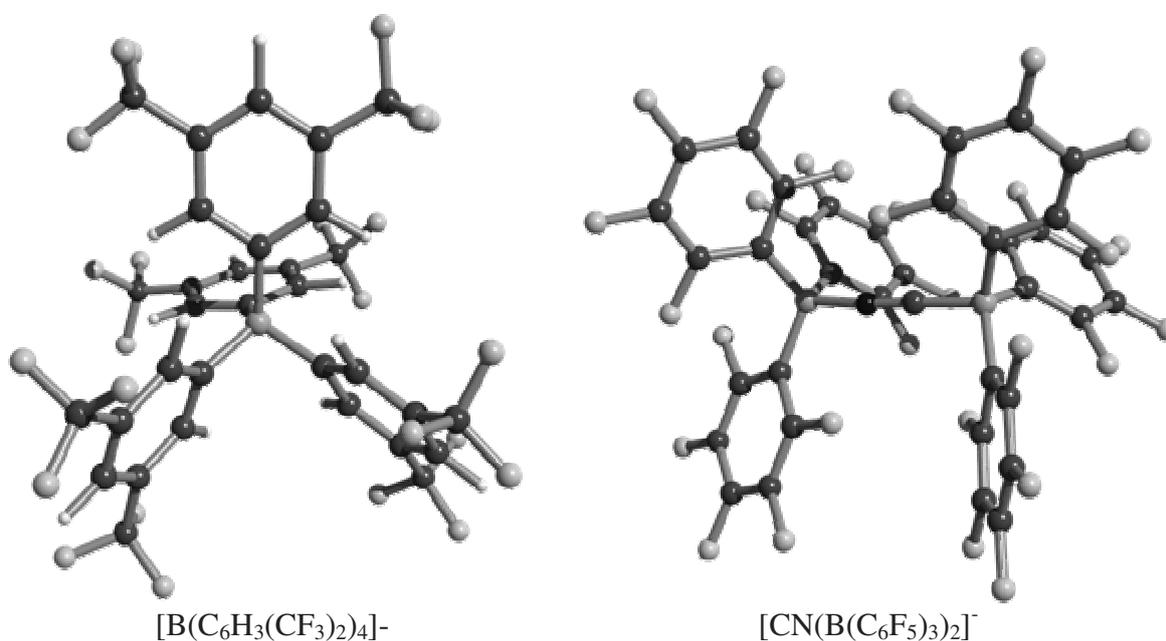


Figure 2. Structures of selected borate based WCAs as ball and stick models.

Similarly to the alkyl borates, substitution of the fluorine atoms in BF_4^- and MF_6^- anions by the larger teflate groups $OTeF_5$ led to the large and robust $[B(OTeF_5)_4]^{-[30]}$ and $[M(OTeF_5)_6]^-$

(M = As,^[31] Sb,^[31-33] Bi,^[31] Nb^[33, 34]), in which the negative charge is dispersed over 20 and 30 fluorine atoms respectively (Figure 3).

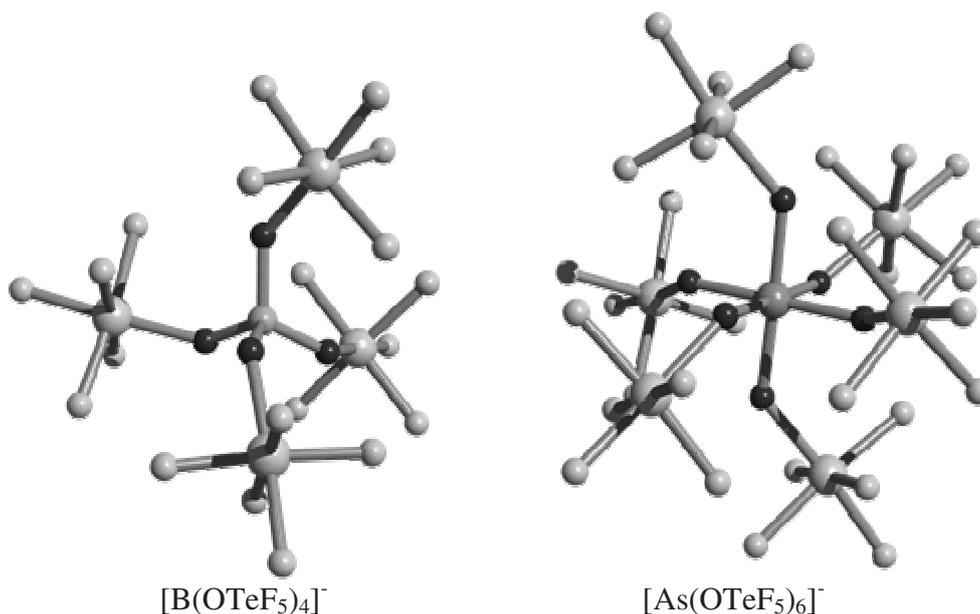


Figure 3. Structures of the teflate based anions [B(OTeF₅)₄]⁻ (left) and [As(OTeF₅)₆]⁻ (right) as ball and stick models.

Generally, the group 15 metallates [M(OTeF₅)₆]⁻ (M = As, Sb, Bi) appear to be more stable than the borate [B(OTeF₅)₄]⁻^[30, 33] However, all teflate based WCAs require the strict exclusion of moisture and decompose rapidly in the presence of traces of moisture.

An alternative to the anions based on a Lewis acidic central atom is the use of a stable univalent polyhedral central moiety such as that of the *closo*-carbaborates [CB₁₁H₁₂]⁻ or [CB₉H₁₀]⁻. Although the exohedral B-H bonds in these anions are very stable and only weakly coordinating, oxidation occurs easily. Therefore, during the last decade several groups tried to improve these anions by substitution of the H atoms with halides or methyl groups. This led to a variety of halogenated and (trifluoro)methylated carbaborates with the general form [CB₁₁X_nH_{12-n}]⁻ (n = 0-12, X = F, Cl, Br, I, CH₃, CF₃)(Figure 4).^[4, 35]

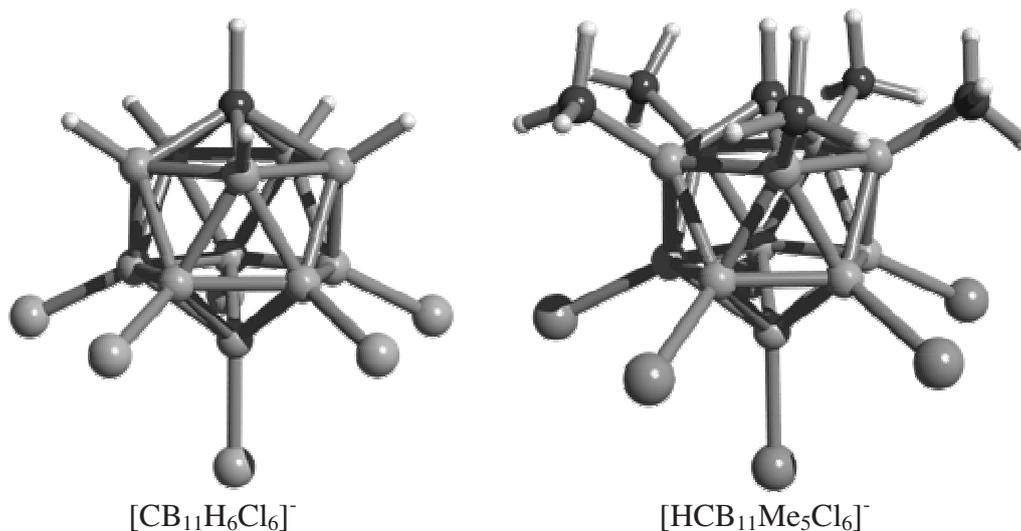


Figure 4. Structures of the carbaborates $[\text{CB}_{11}\text{H}_6\text{Cl}_6]^-$ (left) and $[\text{HCB}_{11}\text{Me}_5\text{Cl}_6]^-$ (right) as ball and stick models.

Despite being very robust as well as weakly coordinating, carbaborates are not widely used due to the expensive and time consuming multistep procedure of their preparation. However, very recently a simple and straight forward high yield two step process giving the $\text{CB}_{11}\text{H}_{12}^-$ anion starting from NaBH_4 , CHCl_3 , base and $\text{BF}_3\cdot\text{OEt}_2$ ^[36] was published. This may open the door for wide applications of the halogenated carborane anions.

Throughout the present work, fluorinated alkoxy aluminates of the formula $[\text{Al}(\text{OR}^{\text{F}})_4]^-$ were almost exclusively used. These anions are representatives of the $[\text{M}(\text{OR}^{\text{F}})_n]^-$ ^[18, 37-40] and $[\text{M}(\text{OAr}^{\text{F}})_n]^-$ ^[41] ($\text{M} = \text{B}, \text{Al}, \text{Nb}, \text{Ta}, \text{Y}$ and La) series of WCAs (Figure 5).

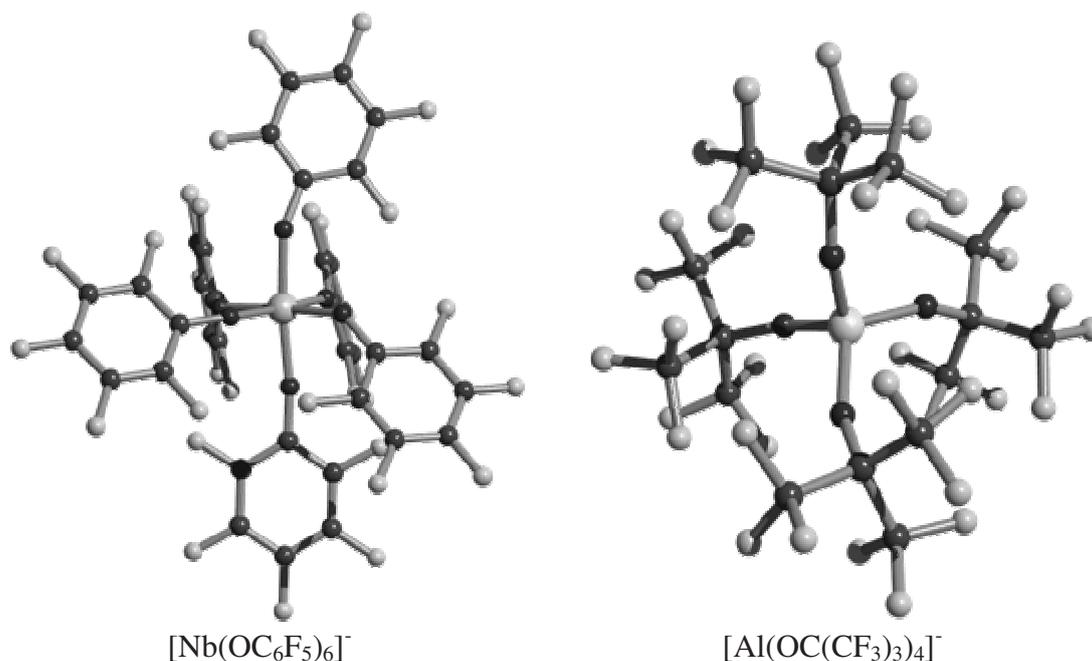


Figure 5. Structures of the fluorinated alkoxy- and aryloxy-metallates $[\text{Nb}(\text{OC}_6\text{F}_5)_6]^-$ (left) and $[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^-$ (right) ball and stick models.

With the large number of peripheral C-F bonds (36 in total), $[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^-$ is, together with $[\text{CB}_{11}(\text{CF}_3)_{12}]^-$, presumably the least coordinating anion known. However, the carborane anion is explosive. In contrast to the normally easily hydrolyzed alkoxy aluminates, the $[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^-$ anion is stable in 6N nitric acid.^[38] This stability towards hydrolysis was attributed to steric shielding of the oxygen atoms, provided by the bulky $\text{C}(\text{CF}_3)_3$ groups, as well as to electronic stabilization due to perfluorination. Stability against electrophilic cations as well as weakly coordinating ability may be further improved with the closely related but even bulkier fluoride bridged $[\text{((F}_3\text{C})_3\text{CO})_3\text{Al-F-Al}(\text{OC}(\text{CF}_3)_3)_3]^-$ anion that has been recently synthesized.^[42] The electron withdrawing effect of the fluorinated ligand can be demonstrated by the increased acidity of the fluorinated $\text{HOC}(\text{H})(\text{CF}_3)_2$ ($\text{p}K_{\text{a}} = 9.5$) and $\text{HOC}(\text{CF}_3)_3$ ($\text{p}K_{\text{a}} = 5.5$) alcohols in comparison to the non fluorinated $\text{HOC}(\text{CH}_3)_3$ ($\text{p}K_{\text{a}} = 19.3$).^[39] Thus, perfluoro^tbutanol is 14 orders of magnitude more acidic than non fluorinated ^tbutanol.

One of the major advantages of these aluminates is that they are easily accessible on a preparative scale: they can be prepared with little synthetic effort on a 100 g scale with well

over 95% yield within two days in common inorganic / organometallic laboratories; Li[Al(OC(CF₃)₃)₄] is also commercially available (Strem Chemicals, USA).

With the variety of different anions developed throughout the last 20 years, the question arises, why they are necessary to stabilize certain target cations. The answer to this question will be sketched now in the 2nd part of this section on the basis of simple thermodynamic Born-Fajans-Haber cycle considerations.

Gas phase cations in condensed phases?

WCAs may be used to crystallize salts of gas phase cations and help to verify the delicate quantum chemical calculations of these cations that often reside in shallow minima on an extended potential energy surface such as Ag(P₄)₂⁺. Initial calculations suggested a Ag(η¹-P₄)₂⁺ to be the global minimum.^[43] whereas a crystal structure revealed η² coordination of P₄.^[44, 45] This example clearly shows that conclusions drawn from gas phase studies are delicate and, if possible, should be validated in the condensed phase.

However, the introduction of an anion (and usually also a solvent) in condensed phases is connected with the lattice energy (E_{Latt}), which influences most strongly the properties of any salt. Since the element differentiating the gas phase and solid state conditions are the anion-cation interactions - the major interaction in the solid state is the strong electrostatic field that results from the close contact of the charged species. According to the simple Kapustinskii equation (eq. 1)^[46] the lattice energies are inversely proportional to the sum of the ionic radii (or volumes in the modified Jenkins equation)^[47] of the constituting ions,^[47] thus the larger the ions, the lower is the lattice energies of the salts, and the less is the electrostatic interaction between them.

$$U = -\frac{120200 \cdot \nu \cdot z^+ \cdot z^-}{r^+ \cdot r^-} \left(1 - \frac{34.5}{r^+ \cdot r^-} \right) \text{kJ mol}^{-1} \quad (1)$$

U = lattice energy, r^+ , r^- = ionic radii of the ions; ν = a number of ions in the unit formula; z^+ , z^- = charge of the ions

For salts with large anions, the lattice energies are very low in comparison to classical salts like Li^+F^- or Cs^+F^- . In fact, they are so low that the lattice energy of the WCA salt $\text{Ag}(\text{S}_8)_2^+[\text{Al}(\text{OR}^{\text{F}})_4]^-$, **I**, ($\text{R}^{\text{F}} = \text{C}(\text{CF}_3)_3$) in Table 1 approaches the values of the sublimation enthalpies of molecular solids of comparable atomic weight, i.e. that of C_{60} or C_{70} of 175 and 200 kJ mol^{-1} (cf. $M_{\text{r}}(\mathbf{I}) = 1588$ vs. 721 (C_{60}) and 841 (C_{70}) g mol^{-1}).^[48-50] Other interactions like dispersive van der Waals, dipole-dipole interactions etc. are of at least one order of magnitude smaller than the lattice energies and, therefore, can be neglected in this 0th order approach.

Table 1. Thermochemical volume and lattice potential energies of several M^+X^- salts.

Salt	$V_{\text{therm}} [\text{\AA}^3]$	$U_{\text{pot.}} [\text{kJ mol}^{-1}]$
Li^+F^-	27	1036 ⁱ⁾
Cs^+F^-	43	740 ⁱ⁾
$\text{Cs}^+[\text{AsF}_6]^-$	128	568 ⁱⁱ⁾
$\text{Cs}^+[\text{Al}(\text{OR}^{\text{F}})_4]^-$ ⁱⁱⁱ⁾	776	362 ⁱⁱ⁾
$\text{Ag}(\text{S}_8)_2^+[\text{Al}(\text{OR}^{\text{F}})_4]^-$ ⁱⁱⁱ⁾	1169	326 ⁱⁱ⁾

ⁱ⁾ experimental value^[49]; ⁱⁱ⁾ calculated from $V_{\text{therm.}}$ ^[47]; ⁱⁱⁱ⁾ $\text{R}^{\text{F}} = \text{C}(\text{CF}_3)_3$.

Comparing the lattice energy of $\text{Ag}(\text{S}_8)_2^+[\text{Al}(\text{OR}^{\text{F}})_4]^-$ to the lattice energies of typical salts such as Li^+F^- and Cs^+F^- clearly shows that the environment of the ions in $\text{Ag}(\text{S}_8)_2^+[\text{Al}(\text{OR}^{\text{F}})_4]^-$ more closely resembles to the situation in the gas phase (or a molecular solid) than the strong electrostatic field within a classical salt like Li^+F^- or Cs^+F^- . Further more, large WCAs have diameters in the nanometer scale, i.e. 1.25 nm for $[\text{Al}(\text{OR}^{\text{F}})_4]^-$ ^[38] or 1.20 nm for

$[\text{Sb}(\text{OTeF}_5)_6]^-$,^[33] and thus considerably separate anions and cations, which effectively diminishes coulombic interactions. Due to the highly fluorinated surface of most WCAs and the very low polarizability of elemental-fluorine bonds, dispersive interactions are weak and not structure determining. Therefore, the environment of the cations within the framework of an ensemble of large and very weakly-coordinating anions may be called "*Pseudo Gas Phase Conditions*" in the solid state.^[48]

The situation in solution is similar: While salts with smaller anions are usually only soluble in polar media with high dielectric constants such as ethanol ($\epsilon_r = 24$), CH_3CN ($\epsilon_r = 35$), water ($\epsilon_r = 81$), or even strong acids such as anhydrous HF ($\epsilon_r = 83$), WCA salts are generally well soluble in rather unpolar solvents with low dielectric constants such as toluene or CH_2Cl_2 ($\epsilon_r = 2$ and 9 respectively).^[49] In these low dielectric media solutions, the solvation energies that stabilize the dissolved ions with respect to the gas phase are greatly reduced (see Figure 6 for a plot of the free solvation energy versus the dielectric constant of the solvent).

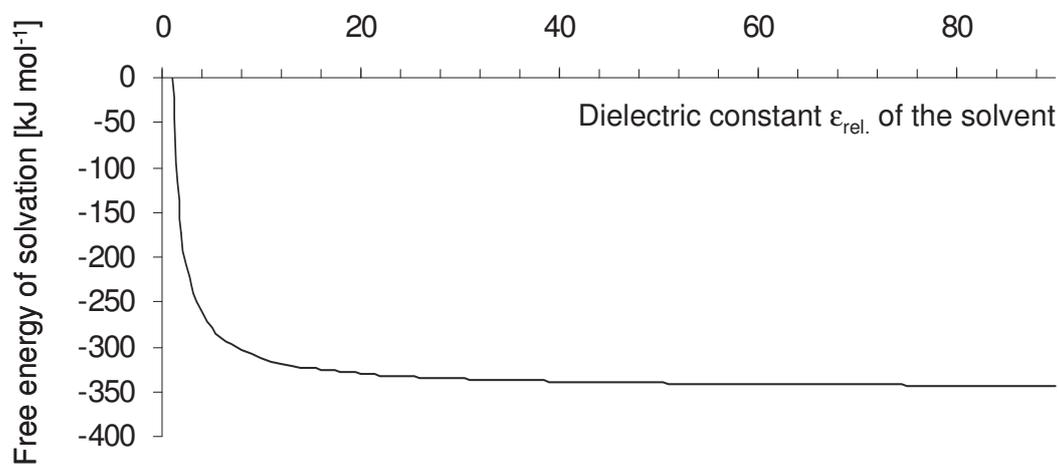


Figure 6. Plot of the free solvation energy calculated with the Born equation for an univalent ion of radius 200 pm versus the dielectric constant of the solvent.

From Figure 6 it may be noted that the effect of decreasing ϵ_r of the solvent from HF ($\epsilon_r = 83$) to ethanol ($\epsilon_r = 24$) is much smaller than for changing ethanol for CH_2Cl_2 ($\epsilon_r = 9$) or toluene ($\epsilon_r = 2$): in low dielectric media only a minimal stabilization by solvation energies is provided