

1. Chemistry with weakly coordinating anions - Introduction and overview

“Begin at the beginning,” the King said, very gravely, “and go on till you come to the end: then stop.”

A very important aspect in the field of chemistry deals with understanding the fundamental nature of interactions between atoms, ions and molecules. While quantum chemical simulations often deliver reliable predictions and are already quite cost-effective, larger systems or systems containing weak interactions still pose problems. For example, it is unimaginable to run molecular dynamics simulations with highly flexible basis sets on the coupled cluster level of theory, simply because the memory and time requirements cannot be met by modern computers. Thus, chemical experiments are necessary because of hardware limitations and inaccuracies in the models. The work of experimentalists is needed to shed some light on selected systems in order to improve the theories.

Among these systems are highly electrophilic cations or complex cations that are held together by extremely weak interactions. These can often be observed in the gas phase in a mass spectrometer, in a solid argon matrix, or predicted by ab-initio calculations. The challenge posed to the synthetic chemist by spectroscopists and theoreticians is to reproduce their results under laboratory conditions, thereby checking if the models are feasible. Pushing the boundaries is not only of academic interest, but makes syntheses of so far inaccessible reactive species possible that could find their way into practical applications. Some prominent examples include the $\text{C}(\text{CH}_3)_3^+$ cation^[1-3] and the halocarbonium ions CX_3^+ ,^[4-7] which are well known in the gas phase^[8-10] and could recently be fully characterized in solution by NMR and in the solid state by X-ray diffraction with the help of weakly coordinating anions. An example for a weakly bound Lewis-acid-Lewis-base complex cation is $[\text{Ag}(\text{P}_4)_2]^+$. This ion has been characterized in 1995 through mass spectrometry, and subsequent calculations predicted a minimum geometry with η^1 coordination of the P_4 units.^[11] However, this is not true in the solid state, as could be shown by the crystal structure of a salt of the same cation, in which P_4 is η^2 -coordinated.^[12, 13] This example shows that conclusions drawn from gas phase studies should be validated in the solid state, if possible.

Further spectacular results, many of which have found their way into modern textbooks, include the stabilizations of cations like Xe_2^+ ,^[14] N_5^+ ^[15] and HC_{60}^+ ^[16].

It becomes clear that such cations must be partnered with a suitable anion that is ideally non-coordinating and not distorting the cation's geometry. Unfortunately, true non-coordination is not possible, because any confined system must be charge-neutral. For every positive charge created, an equal negative charge must exist somewhere; everybody intuitively understands that opposed charges interact with each other. Yet it is possible to find anions which help to replace few strong cation-anion interactions by many very weak ones, ideally placing the cation in a field of weak interactions that mostly cancel each other out. These are called "weakly coordinating anions" (WCAs) and are sometimes also referred to as "spectator anions" because ideally, they play no role in reactions of their partner cation. To be weakly coordinating, an anion must possess a very low nucleophilicity and basicity. A high stability versus oxidation and strong electrophiles is necessary to prevent degradation, thus the WCA should be formed of chemically robust moieties. Finally, its negative charge should be delocalized over a large surface, because sites that offer a significantly higher charge concentration than the rest of the surface would be primary locations of electrophilic attack. Several classes of weakly coordinating anions are known, which shall be briefly introduced in the following sections along with a short description of their suitability for various applications.

Fluorometallate anions

Anions of the type $[\text{MF}_6]^-$ ($\text{M} = \text{Sb}, \text{As}$) can be introduced by metathesis with their Li^+ or Ag^+ salts, which are prepared by reacting M_2O_3 with bromine trifluoride and LiF or AgF .^[17] A more practical approach is the in situ generation of fluoride bridged fluorometallates, as MF_5 are among the strongest Lewis acids; in weakly basic media like anhydrous HF , SO_2 , SO_2ClF or SbF_5 , larger and less coordinating oligomeric species of the general type $[\text{M}_n\text{F}_{5n+1}]^-$ can be directly obtained by fluoride abstraction (Fig. 1). The $[\text{As}_2\text{F}_{11}]^-$ anion has been known for a long time, but was only recently structurally verified.^[18-22]

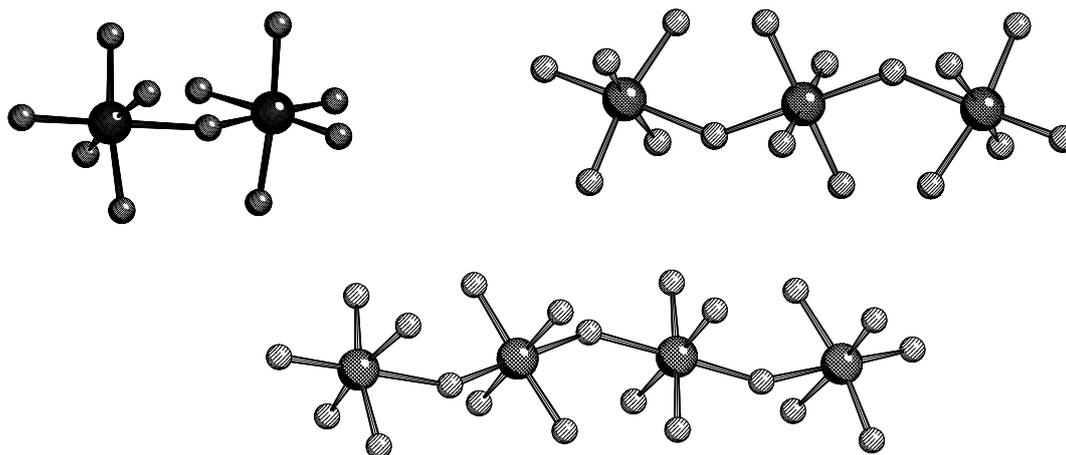


Fig. 1: Structures of $[\text{Sb}_2\text{F}_{11}]^-$ (top left), $[\text{Sb}_3\text{F}_{16}]^-$ (top right) and $[\text{Sb}_4\text{F}_{21}]^-$ (below).

Anions of this type are very robust against decomposition and a variety of extremely electrophilic cations could be stabilized with their help, including Br_2^{+23} and Xe_2^{+14} , as well as weakly bound adducts like $[\text{Au}(\text{Xe})_n]^+$ ($n = 1, 2, 4$).^[24, 25] However, $[\text{M}_n\text{F}_{5n+1}]^-$ salts can only be handled in specialized fluorine laboratories, restricting application to the elucidation of textbook cations. Furthermore, $[\text{M}_n\text{F}_{5n+1}]^-$ exist in solution only as mixtures with varying n (1-4), leading to difficulties during crystallization. The free Lewis acids MF_5 act as strong oxidizing agents, which may give rise to unwanted side reactions.

Borate and related anions

Another type of WCAs consists of boron-centered anions, which can be very stable because boron forms very strong B-C bonds with a large variety of ligands. Among the most well-known complex anions in this class are tetrafluoroborate $[\text{BF}_4]^-$ and tetraphenylborate $[\text{BPh}_4]^-$. Both are strongly coordinating and suffer from a low stability; $[\text{BF}_4]^-$ tends to decompose into F^- and BF_3 and $[\text{BPh}_4]^-$ is prone to hydrolysis.^[26, 27] These problems can be overcome if fluorinated groups are introduced as in the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ^[28] and $[\text{BAr}^{\text{F}}_4]^-$ ($\text{Ar}^{\text{F}} = \text{C}_6\text{H}_3\text{-}3,5\text{-(CF}_3)_2$)^[29, 30] anions (Fig. 2); several salts of both are commercially available. Especially the $[\text{BAr}^{\text{F}}_4]^-$ anion is widely used, e.g. in homogenous catalysis.^[31]

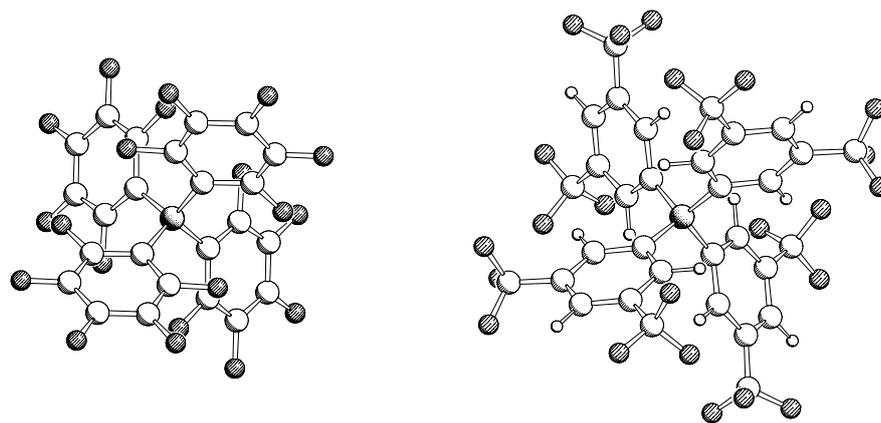


Fig. 2: Structures of the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (left) and $[\text{BAr}^{\text{F}}_4]^-$ ($\text{Ar}^{\text{F}} = \text{C}_6\text{H}_3\text{-3,5-(CF}_3)_2$, right) anions.

The ligands can be modified to achieve higher stability, weaker coordination and better solubility in unpolar solvents, resulting in anions like $[\text{B}((\text{C}_6\text{H}_3)\text{-3,5-(R}^{\text{F}})_2)_4]^-$ ($\text{R}^{\text{F}} =$ perfluorinated alkyl group),^[32, 33] $[\text{B}(\text{C}_6\text{F}_4(\text{CF}_3))_4]^-$,^[34] $[\text{B}(\text{C}_6\text{F}_4(\text{Si}(\text{iPr})_3))_4]^-$,^[35, 36] $[\text{B}(\text{C}_6\text{F}_4(\text{SiMe}_2^t\text{Bu}))_4]^-$ ^[35, 36] or $[\text{B}(\text{C}_6\text{F}_4(\text{CF}(\text{C}_6\text{F}_5)_2))_4]^-$.^[37] It is also possible to exchange the boron atom for aluminum or gallium, but the resulting anions are very unstable versus hydrolysis, and the aluminum species tend to be explosive.^[38] Another approach is to react the parent Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ with a strong nucleophile X^- like CN^- ^[39], NH_2^- ^[40], or $\text{C}_3\text{N}_2\text{H}_3$ ^[41] to obtain boron-bridged anions of the type $[\text{X}(\text{B}(\text{C}_6\text{F}_5)_3)_2]^-$ (Fig. 3), which are very stable and easily prepared.

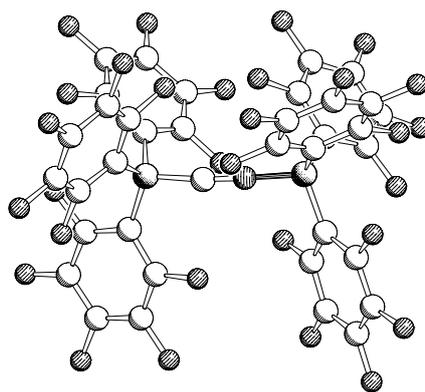


Fig. 3: Structure of the $[(\text{F}_5\text{C}_6)_3\text{B}(\mu\text{-CN})\text{B}(\text{C}_6\text{F}_5)_3]^-$ anion.

Smaller borate anions include $[\text{B}(\text{CF}_3)_3]^{-}$ ^[42-45], $[\text{B}(\text{CF}_3)_4]^{-}$ ^[46-48] and tetracyanoborate $[\text{B}(\text{CN})_4]^{-}$ ^[49, 50] (Fig. 4), the latter being able to stabilize $[\text{C}_6\text{F}_5\text{Xe}]^+$.^[49] $[\text{B}(\text{CF}_3)_4]^{-}$ is very stable (against Na in liquid ammonia and against elemental fluorine in anhydrous HF) and its coordinative strength is small enough to form $[\text{Ag}(\text{CO})_n]^+[\text{B}(\text{CF}_3)_4]^{-}$ ($n = 3, 4$) from the silver salt at high CO pressure.^[46]

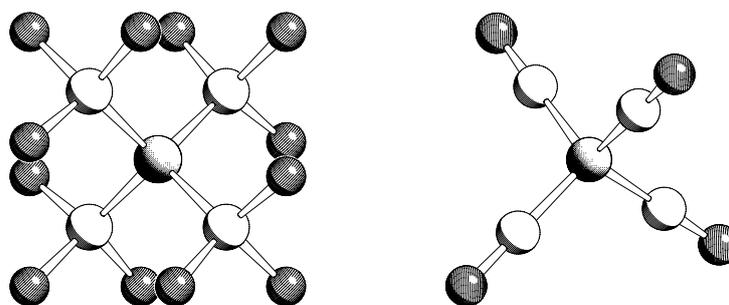


Fig. 4: Structures of the $[\text{B}(\text{CF}_3)_4]^{-}$ (left) and $[\text{B}(\text{CN})_4]^{-}$ (right) anions.

Alkoxy- and aryloxymetallates

Similar in structure to the borate anions are metallates of the general formula $[\text{M}(\text{OR}^{\text{F}})_n]^{-}$ (Fig. 5, R^{F} = poly- or perfluorinated alkyl or aryl group, $\text{M} = \text{Al}^{\text{III}}, \text{Nb}^{\text{V}}, \text{Ta}^{\text{V}}, \text{Y}^{\text{III}}, \text{La}^{\text{III}}$).^[51-56]

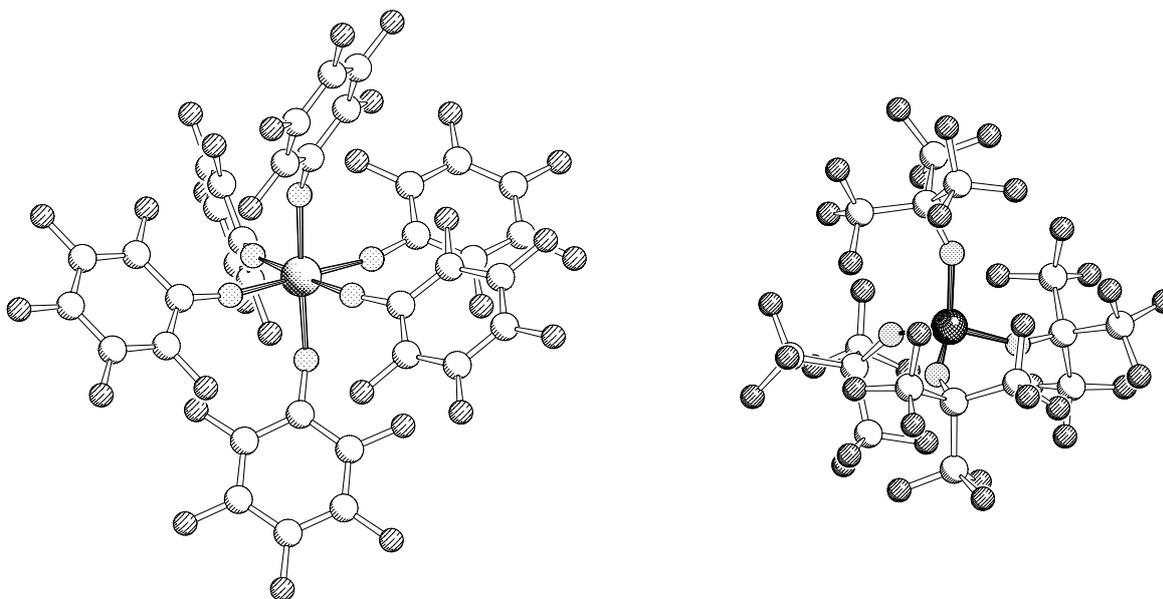


Fig. 5: Structures of $[\text{Nb}(\text{OC}_6\text{F}_5)_6]^{-}$ (left) and $[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^{-}$ (right).

Salts of $[M(OR^F)_n]^-$ are easily accessible even in larger scales. Some of these anions have successfully been tested as counterions in cationic polymerization reactions.^[34, 57, 58] Especially the introduction of sterically demanding ligands like $OC(CF_3)_3$, $OC(CH_3)(CF_3)_2$ or $OCH(CF_3)_2$ has led to alkoxyaluminate anions that are well suited for many purposes.^[53, 54] $[Al(OC(CF_3)_3)_4]^-$ is among the most weakly coordinating anions currently known (due to the high number of peripheral C-F bonds), comparable with the carboranate $[CB_{11}(CF_3)_{12}]^-$ (cf. later in this chapter), which has the disadvantage of being explosive and suffers from an extremely tedious synthetic route with low yields.^[59] The Li^+ salt of the aluminate is available in 100 g scale with over 95 % yield from commercially available starting materials and is even stable in water and boiling aqueous nitric acid (35 weight %).^[53] This high stability arises from the steric shielding of the basic oxygen atoms by the bulky ligands with perfectly interlocking $-CF_3$ groups and the electronic stabilization resulting from perfluorination. Consequently, the $[Al(OC(CF_3)_3)_4]^-$ anion can be used to stabilize very reactive cations like $[H(OEt)_2]^+$,^[60] Cl_3^+ ,^[4] $[Ag(P_4)_2]^+$,^[12] PX_4^+ , $P_2X_5^+$, $P_5X_2^+$ ($X = Br, I$),^[61, 62] $AsBr_4^+$ ^[63] and many more. In analogy to the bridging in $[M_nF_{5n+1}]^-$ and some borates, the stability is further improved in the fluoride-bridged $[F\{Al(OC(CF_3)_3)_3\}_2]^-$ anion (Fig. 6), in which the negative charge is distributed across 54 peripheral C-F bonds.^[64] This species was first discovered as a decomposition product from $[Al(OC(CF_3)_3)_4]^-$ in reactions with very reactive cations like PX_2^+ ($X = Cl, Br, I$),^[62, 65] but can also be synthesized directly in a planned synthesis in 100 g scale. As will be discussed later in this chapter, the increase in size also induces a lower coordinative strength compared to $[Al(OC(CF_3)_3)_4]^-$. Alkoxyaluminate anions of various types were almost exclusively used in the practical work presented in this thesis, and some of their characteristics will be described in more detail in later chapters.

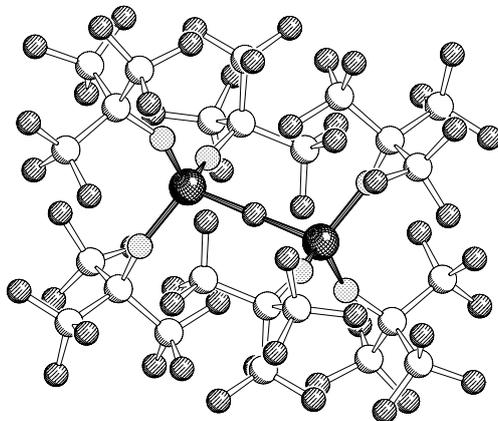


Fig. 6: Structure of the fluoride-bridged $[F\{Al(OC(CF_3)_3)_3\}_2]^-$ anion.