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The Coordination Chemistry of the CF Unit in Fluorocarbons

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Contents

I. Introduction

The title of this article may sound paradoxical, since the first idea about fluorine in coordination chemistry is that of being a common constituent of large and very weakly coordinating anions.[1] To find support for this view one only needs to consult recent review articles by Strauss,[2] Bochmann,[3] Seppelt,[4] Lawrance,[5] or Beck[6] for numerous examples of fluorinated inorganic or organic anions such as PF_6^-, AsF_6^-, SbF_6^-, FSO_3^-, $OTeF_5^-$, $CF_3SO_3^-$, and $B(C_6F_5)_4^-$. However, before abandoning the idea of CF units as donors for metal ions, it is worth considering what properties make atoms such as oxygen, nitrogen, or sulfur good donors in ligands such as ethers, amines, or thioethers.[7] This may be done in the simple terms of the concept of hard−soft−acid−base interactions presented by Pearson.[8] Accordingly, atoms of lower electronegativity such as sulfur are classified as soft donors, while highly electronegative oxygen is the most important example of a hard donor center, best suited to form complexes with equally hard metal ions. This hardness of oxygen also implies that the interaction between ligand and metal ion has a significant electrostatic component as was shown recently by Glendening et al. for the alkali metal cation complexes of 18-crown-6.[9] Consequently the high electronegativity of fluorine, its small size, and its hardness raise the idea of CF units in fluorocarbons as promising donors for metal ions. This notion seems very close at hand, but obviously must have failed to impress the chemists and hence the first detailed investigation on the coordination chemistry of CF units was published as late as 1983 in a landmark paper by Glusker, Murray-Rust et al.[10] As a result of a systematic search in the Cambridge Structural Database (CSD) the authors had found seven crystal structures of group I and II metal salts in which exceptionally short contacts between the metal ions and CF units were observed. These

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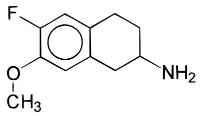

Figure 1.

findings led Glusker to finally conclude as a result of her studies: "We believe that the C−F bond is capable of significant, if not prominent, interactions with both alkaline metal cations and proton donors."

Consequently there was little doubt about the existence of CF···metal interactions in the solid state, but it was far from clear whether such contacts would persist in solution. Evidence supporting this was presented by Davidson et al. in 1989 in thallium complexes with the $CpMo(C_6F_5)_4$- ligand.[11] However, in this system CF···metal contacts only occur in less polar solvents and it appears likely that CF···metal contacts mainly result from the formation of close ion pairs between negatively charged ligands and cationic metal centers. More recently Plenio and Diodone presented clear evidence for the stabilizing effect of CF coordination in solution as well as in the solid state, by investigating group I and group II metal complexes of neutral fluorine-containing macrocycles.[12] In recent years it has been realized that CF···metal coordination is more general and a few examples will be presented in the following paragraphs.

One area of very active research is the homogenous olefin polymerization of the Ziegler−Natta type based on metallocene catalysts, which is on the verge of breakthrough for large-scale technical applications. However, a major shortcoming of the current process is the need for a large excess of the methylalumoxane (MAO) cocatalyst with respect to the zirconocene, in order to generate the highly active cationic catalysts. Alternatively the stabilization of the cationic metallocenes is possible with $B(C_6F_5)_4^-$ (or related anions) as a counter ion. However, this anion is not an innocent bystander and in recent years several examples of CF coordination to the cationic metal centers, which seems to be crucial for catalyst behavior, have been published. Investigations into the coordination chemistry of CF units may also shed some new light on the behavior of fluorine-containing pharmaceuticals,[13] since body fluids contain fairly large concentrations of alkali and alkaline earth metals ions, notably Na^+, K^+, and Ca^{2+}.[14] An example of a potential chelating ligand is the tumor necrose factor blocker shown in Figure 1.

Related to the area of CH activation of hydrocarbons is the CF activation of fluorocarbons by transition metal complexes. This field was recently reviewed by Richmond et al.[15] and Crabtree et al.[16] and will therefore not be discussed here. Consequently this article is limited to chemistry in which the CF bond remains intact. Some of the aspects of CF···metal coordination have previously been dealt with in a review by Kulawiec and Crabtree on the coordination chemistry of halocarbons,[17] with Richmond et al. giving an update.[15]

Another interesting detail of the participation of CF units in metal binding is that the ^{19}F nucleus displays excellent NMR spectroscopic characteristics,[18] which are in stark contrast to the NMR behavior of other hard donor atoms such as the low abundance ^{17}O or ^{15}N isotopes. ^{19}F NMR spectroscopy could therefore become a powerful tool for gaining a deeper understanding of the coordination chemistry of hard metal ions in solution or for studying supramolecular association processes.[19] Previous NMR work in group I and II chemistry, pioneered by Popov [20] and Detellier,[21] had to rely on a few suitable NMR nuclei such as $^{6,7}Li$, ^{23}Na, and ^{133}Cs, while knowledge about the coordination chemistry of the alkaline earth metal ions in solution has remained limited.

II. Scope of This Review

In the majority of complexes to be described in this review, the existence of close CF···metal interactions was proven by X-ray crystal structure analyses. The number of studies focused on obtaining solution information by various spectroscopic techniques (mainly NMR spectroscopy) is rather limited, but will be presented in more detail than would be appropriate regarding the small number of publications. Consequently the review of references dealing with the influence of CF···metal interactions on stereo- and regioselective organic synthesis is also attempted.

In order to locate X-ray crystal structures with short metal−fluorocarbon interactions a CSD search was performed.[22] In the following discussions, prior to the description of each group of metals, the criteria described were applied to select the CSD data in the search for possible CF···metal interactions. It should, however, be noted that any bond length threshold set for screening and selecting the data sets will be arbitrary, which is well illustrated by the continuing discussion and revision of ionic radii, van der Waals radii, or covalent radii.[23] The difficult task is to set up reasonable distance thresholds for CF···metal interactions, since it is not considered a good idea to use to the sum of the van der Waals radii of fluorine and the respective metal involved, as is often done in the literature. This approach is not appropriate when one considers the complexes of hard metal ions and provides much too loose a criterion. Conversely, for covalent complexes, ionic radii are questionable and van der Waals radii may be more appropriate. As a consequence of these basic considerations it was decided to individually evaluate each group of metals with respect to a reasonable distance threshold.

In addition to such distance limits one general restriction was applied: For intramolecular metal−fluorine interactions to be accepted as such, there must be a minimum of four bonds separating the two atoms. This eliminates metal complexes of fluorinated ligands such as η^1-C_6F_5, η^6-C_6F_6,[24] $-CF_3$, $=CF_2$, $F_2C=CF_2$, and related fluorocarbons[25] as well as carbenoids.[26] It is very possible that the presence of fluorine in the complexes with such ligands is stabilizing, but it should also be considered that such contacts are the unavoidable result of the existence of such metal complexes.

The main section of this review deals with alkali and alkaline earth metal complexes of fluorinated ligands. In the transition metal series by far the most important metals in the context of this review are zirconium and silver. Although only a few examples from the lanthanide−actinide series are known, a large section reports on complexes of the heavy main group metals, followed by a presentation of the latest results on possible CF···HN hydrogen bonds. The literature until June 1997 is covered.

Table 1. Metal−Oxygen and Metal−Fluorine Bond Parameters[a]

	d_{av}[a]	stretch[b]	d_{MO}[c]	r_{ion} (c.n.)[d]	d_{min}[e]	d_{max}[f]
Li^+	226	−17/ +29	205	59 (4)	206	247
Na^+	252	−20/ +34	238	102 (6)	249	307
K^+	283	−22/ +38	275	151 (8)	298	347
Rb^+	295	−24/ +42	292	166 (10)	313	367
Cs^+	319	−24/ +43	310	181 (10)	328	387
Ca^{2+}	251	−15/ +23	240	106 (6)	253	313
Sr^{2+}	268	−16/ +26	258	126 (8)	273	330
Ba^{2+}	287	−17/ +29	283	152 (10)	299	348

[a] d_{av} [pm] is the average metal−oxygen bond length obtained from X-ray crystal structure analyses of crown ether complexes of the respective metal ions.[30] [b] Stretch [pm] is the elongation or shortening of the metal−oxygen bond length resulting from a displacement energy of 1 kcal/mol.[30] [c] d_{MO} [pm] is the strain-free length of the metal−oxygen bonds.[30] [d] r_{ion} [pm] is the ionic radius of the metal ion (according to Shannon[31]) (c.n.= typical coordination number given in brackets). [e] d_{min} [pm] is the sum of the ionic radius of the respective metal ion (r_{ion}) and the van der Waals radius of fluorine (147 pm). [f] d_{max} [pm] is the maximum metal−fluorine distance considered in this study and it is the sum of the van der Waals radii of fluorine (147 pm) and the ionic van der Waals radii by Kollman (the values for Ca^{2+}, Sr^{2+}, and Ba^{2+} are estimates based on the values for Na^+ and K^+).

III. Complexes of the Alkali and Alkaline Earth Metal Ions

Not too long ago chemists could have easily dismissed the coordination chemistry of group I and II metal ions as less interesting. However, as a consequence of the watershed established by Pedersen's discovery of crown ethers[27] and because of the huge impact his new ligands have had since the 1970s, this opinion obviously had to be revised. The availability of coronands, cryptands, and spherands revolutionized this field, also because oxygen atoms in ethers are the ideal donor atoms for group I and II metal ions.[28] If one considers the high electronegativity of oxygen and fluorine, their similarity in size, and the fact that in ethers and in fluorocarbons both atoms carry significant negative partial charges, roughly similar donor characteristics for the two atoms could be expected. Surprisingly, in spite of this the study of coordination chemistry of fluorocarbons has only recently gained momentum.

The most convenient method for identifying CF···metal contacts is X-ray crystal structure analysis, hence the bulk of knowledge gathered on such complexes was obtained using this technique. Prior to extracting information on such interactions from the literature an arbitrary but nonetheless important decision on what to regard as CF···metal interactions had to be made, which will be described in the following paragraphs.[29]

The most obvious choice for such a bond length criterion would be the sum of the van der Waals radii of fluorine (147 pm) and of the respective metal, however, values derived in this manner are extremely large (Li + F = 327 pm, Na + F = 377 pm, K + F = 427 pm). It is apparent that this approach does not make much sense since the CF···metal interactions in the complexes of group I and II metal ions are best described by the interaction of a covalently bonded fluorine with a metal cation. To aid the decision on a useful bond length threshold, a recently developed MM3-based force field for the crown ether complexes of alkali and alkaline earth metal ions by Hay and Rustad was considered useful as a rough guide.[30] In this study the average metal−oxygen bond lengths d_{av} were determined by a CSD search and used to iteratively calculate strain-free metal−oxygen bond lengths d_{MO}, force constants (Table 1), and other relevant parameters describing the metal−ether interaction. One significant result of the calculations was that the potential well of the metal−oxygen bond stretch is rather shallow. Consequently, small displacement energies result in substantial elongations or shortenings of the metal−oxygen distances (Table 1). This is important with respect to CF···metal interactions since because of the expected weaker bonding, it should even be easier to stretch or compress the CF···metal bond length from its ideal length. In this respect the effect of packing forces on the observed CF···M^+ distance should not be underestimated. It is interesting that the d_{MO} values (corresponding to an energy minimum) in Table 1 given by Hay and Rustad are reproduced reasonably well by summing up the respective ionic radii of the metal ions (with typical coordination numbers)[31] and the van der Waals radii of fluorine or oxygen $d_{min} = r_{ion} + r_{vdW}(F)$ (Table 1).

A bond length threshold up to which CF···metal interactions are eligible for this section might now be derived by allowing a certain (arbitrary) variation in the d_{min} values. This approach is prone to criticism and therefore a more convincing concept had to be applied. Kollman has introduced ionic van der Waals radii for the alkali metal ions and it appears sound to use his data for our purpose.[32,33] Consequently the sum of Kollman's ionic van der Waals radii and the van der Waals radius of fluorine which are listed in Table 1 as d_{max} are taken as upper limits up to which X-ray data are considered for this section.

A. Lithium

The hardest metal ion among the alkali metals is lithium, and it therefore seems well suited for interactions with hard CF units. In addition ^6Li and ^7Li display useful NMR spectroscopic properties which offer the chance to observe fluorine−lithium coupling constants in suitable complexes. Nevertheless, relatively few compounds with CF···Li^+ interactions have been described in the literature.

The earliest such example was reported as late as 1988 by Klingebiel et al. who observed a short CF···Li^+ interaction of 227.3(10) pm for the C_6F_5 ring of $^tBu_2FSiN(Li)C_6F_5\cdot(thf)_2$ (KAKZEB) (Figure 2) together with a second slightly longer SiF···Li^+ contact of 238.6(10) pm.[34]

Stalke and Whitmire found that intermolecular contacts stabilize $[2,4,6\text{-}(CF_3)_3C_6H_2Li\cdot Et_2O]_2$ (JE-

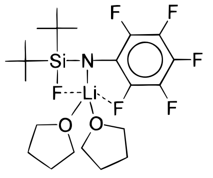

Figure 2. KAKZEB.

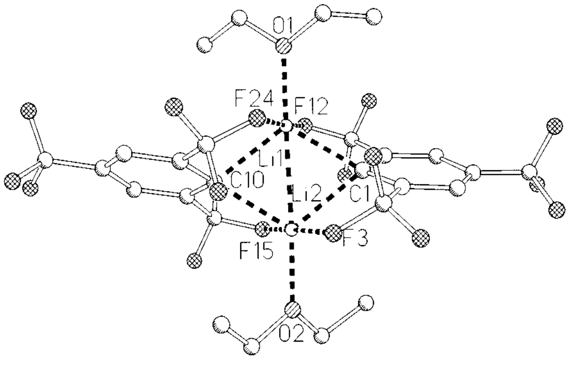

Figure 3. Crystal structure of JEJDIL (hydrogen atoms omitted).

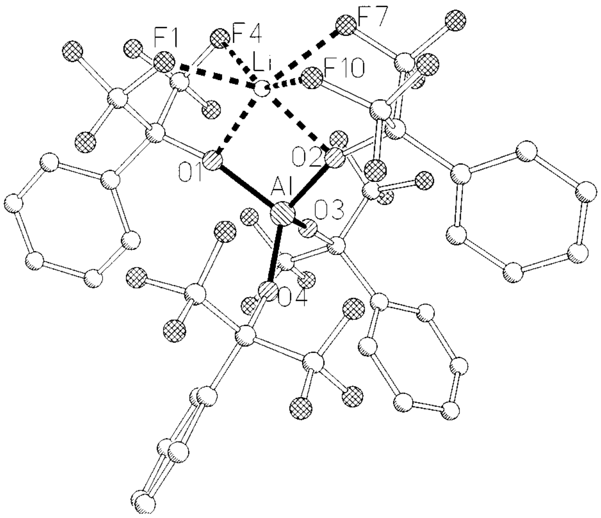

Figure 4. Crystal structure of LiAl[OC(Ph)$(CF_3)_2]_4$ (hydrogen atoms omitted).

JDIL) with CF···Li^+ distances of 224.3(12) and 229.3(12) pm. The $Li(C_2OF_2)$ environment can be viewed as distorted trigonal−bipyramidal (Figure 3).[35]

The exciting hydrocarbon soluble complex LiAl[OC(Ph)$(CF_3)_2]_4$ was recently synthesized by Grieco, Strauss et al. in the reaction of $LiAlH_4$ and HOC(Ph)$(CF_3)_2$ (Figure 4). In the crystal the very unusual $Li(O_2F_4)$ coordination sphere can be described as trigonal prismatic displaying four short CF···Li^+ contacts of 198.4(9), 208.2(9), 209.8(11), and 235.2(9) pm, with the Li−O distances of 197.8(8) and 196.6(8) pm being only slightly shorter.[36] A lengthening of the C−F bonds [129.8(5)−134.2(5) pm] in the lithium bonded CF_3 groups relative to the other C−F bonds [134.1(5)-138.4(5) pm] was attributed to strong CF···Li^+ contacts. This was also evidenced by NMR spectroscopy since the ^{19}F NMR signal consists of four lines with a 2.4 Hz splitting as a result of coupling with ^7Li. Surprisingly, however, all fluorine atoms within the CF_3 groups bonded to lithium are magnetically equivalent, even at low temperatures.

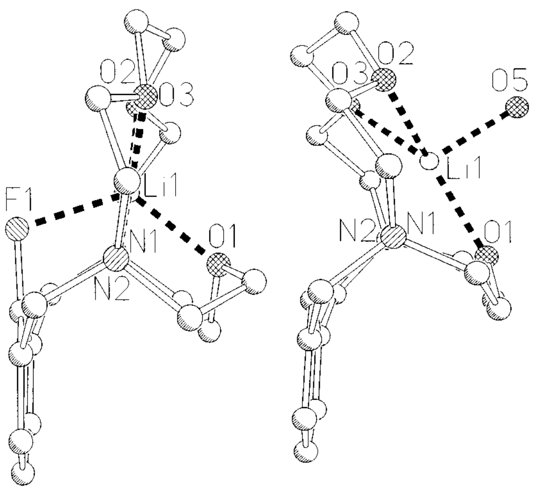

Figure 5. Crystal structure of $FN_2O_3 \cdot Li^+$ (left) and $HN_2O_3 \cdot Li^+$ (right) (hydrogen atoms omitted, O(5) is a water molecule).

The lability of the lithium ion in its unusual ligand environment has a distinct influence on the chemical reactivity of this complex, which turns out to be a highly active catalyst for carbon−carbon bond forming reactions in hydrocarbon solvents. This ready availability of the metal ion for catalytic transformations is consistent with the hemilabile nature of the CF donors bonded to lithium.

Plenio and Diodone reported the crystal structure of a complex with the neutral macrocyclic ligand FN_2O_3 (23-fluoro-4,7,20-trioxa-1,10-diazatricyclo-[8.7.5.1^{12,16}]tricosa-12,14,16(23)-triene, ZOHXOJ) with $LiClO_4$ (Figure 5).[12] The $Li(O_3F)$ coordination sphere in this complex may be viewed as roughly tetrahedral with three Li−O [193.6(5), 201.3(5), 202.1(5) pm] and one CF···Li^+ contact [203.5(5) pm], while the Li−N distances are much longer [239.4(5), 255.5(5) pm]. To better understand the donor properties of the CF unit the fluorine-free ligand HN_2O_3 was synthesized, which differs from FN_2O_3 only with respect to the single fluorine atom which is substituted by a hydrogen atom. A comparison of the X-ray crystal structures of $FN_2O_3 \cdot LiClO_4$ and $HN_2O_3 \cdot LiClO_4$ reveals significant differences (Figure 5). While in the fluorine-containing complex $FN_2O_3 \cdot Li^+$ the metal ion is located in the center of the cavity, it has moved toward the periphery in the fluorine-free complex $HN_2O_3 \cdot Li^+$, coordinating one molecule of water in a trigonal−pyramidal donor array instead of the fluorine donor. The conclusion drawn from these observations is that one donor atom (fluorine) is missing in the HN_2O_3 ligand. In the NMR spectra of $FN_2O_3 \cdot Li^+$ a coupling $J(^7Li-^{19}F) = 19$ Hz is observed. Upon formation of $FN_2O_3 \cdot Li^+$ the ^{19}F NMR resonance shifts by −18.2 ppm with respect to that of the free ligand, which is another indication of close CF···metal interactions in solution. In FN_2O_4, the cavity of which is enlarged by one additional OCH_2CH_2 unit with respect to that of FN_2O_3, Li−F couplings are absent. A more detailed report of the solution behavior of the metal complexes of the fluoro macrocycles with respect to CF···metal interactions will be given in section III.H.

Table 2. Short Formulas/Names of the Complexes (Pz = Pyrazolyl), CSD Refcodes, CF···Na^+ Distances [pm], and Literature References[a]

formula/name	refcode	distance CF···Na^+ [pm][a]	ref
$[Na_2(VO)(CF_3CO_2)_4]_2$	BUXTAP	287.3, 296.4	49
$[(CF_3)_2C{=}NC(CF_3)_2ONa]$	DENZAX	301.5	62
Na-fluoropyruvate	FPYRVH	247.0	50
$[NaOCH(CF_3)_2]_4$	HAGYAP	236.5(2), 241.2(2), 248.1(2), 263.5(2), 263.6(2), 264.1(2), 265.2(2), 269.8(2), 273.7(2), 274.6(2), 280.5(2), 283.1(2), 285.7(2), 292.2(2), 299.4(2), 300.9(2)	37
$Na_2Zr(OCH(CF_3)_2)_6$	HAGYIX	267.6(3), 281.0(3)	37
$Na_2Zr(OCH(CF_3)_2)_6$	HAGYOD	271.8(4)	37
$Na_2[Cu(OCH(CF_3)_2)_4]$	JIWVIU	248.1(7), 248.7(7), 259.0(7), 262.0(7), 278.5(7)	39
Na-monofluoroacetate	NAFLAC	256(2)	43
$[\mu_2\text{-}\{2,4,6\text{-}(CF_3)_3C_6H_2O\}Na(THF)_2]_2$	SISHUX	266.5(7), 271.8(7)	44
$[\mu_2\text{-}\{2,4,6\text{-}(CF_3)_3C_6H_2S\}\ Na(THF)_2]_x$	SISJEJ	243.4(3), 257.3(3)	44
$Na[Mo(C_6F_5)(CO)_2\{P(OMe)_3\}]$	VOVDOZ	243.1(3)	51
$Na_3Y\ [\mu_2\text{-}OCH(CF_3)_2)(THF)_3]_6$	YOXTUA	248.5(8), 250.4(8), 251.5(8), 256.6(8), 262.2(8), 273.6(8), 275.1(8), 280.5(8), 288.4(9), 302.8(8)	40
$Na_2Y[(\mu_2\text{-}C(CH_3)(CF_3)_2)_4\{OC(CH_3)(CF_3)_2\}THF)_3]$	ZAWMEP	240.9(6), 248.8(6), 251.9(6), 252.1(6), 259.0(6), 259.9(6), 262.1(8), 263.4(6), 265.7(6), 285.7(6)	40
$[Na\{\mu_3\text{-}OC(CF_3)_3\}]_4$	ZAQZII	249.8(4), 252.7(4), 260.2(4), 265.2(4), 293.0(4)	38
$[NaOC(CF_3)(CH_3)_2]_4$	–	233.2(5), 263.5(5), 263.7(5), 266.2(5), 277.4(5), 289.9(5), 296.0(5)	38
F_2-[3.1.1]cryptand·$NaCF_3SO_3$	–	229.8(3), 235.7(3)	48
FH-[3.1.1]cryptand·$NaClO_4$	–	236.0(4)	48
$FO_5{\cdot}NaClO_4$	ZOHYEA	237.4(5)	12
$BenzoFN_2O_3{\cdot}NaCF_3SO_3$	–	246.8(2)	47
$FN_2O_3{\cdot}NaClO_4$	ZOHYAW	257.5(2)	12
$FN_2O_4{\cdot}NaCF_3SO_3$	–	267.1(2)	47
$Na[HB\{3,5\text{-}(CF_3)_2Pz\}_3]$	ZUVQOQ	274.4(3), 290.9(2)	46
$Na[HB\{3,5\text{-}(C_2F_5)_2Pz\}_3]$	ZUVQIR	271.5(4), 288.3(6), 292.1(4), 295.7(4)	45
$Na[W_2\{OOCCCo_3(CO)_9\}_2(OOCCF_3)_4\ ]$	–	268(2)	52

[a] Most C–F···Na^+ angles are in the range 100–120°.

B. Sodium

For sodium a large number of X-ray crystal structures with short CF···Na^+ contacts are known and a summary of the X-ray crystallographic work can be found in Table 2.

Caulton et al. and Purdy et al. synthesized a number of sodium salts of the fluorinated alcohols $(CF_3)(CH_3)_2COH$, $(CF_3)_2HCOH$, $(CF_3)_2(CH_3)COH$, and $(CF_3)_3COH$. In the course of these investigations X-ray crystal structures of several sodium salts were determined; one example is shown in Figure 6: $[NaOCH(CF_3)_2]_4$ (HAGYAP),[37] $[NaOC(CF_3)(CH_3)_2]_4$,[38] $Na_2Zr[OCH(CF_3)_2]_6{\cdot}(C_6H_6)_2$,[37] $Na_2Zr[OCH(CF_3)_2]_6{\cdot}C_6H_6$,[37] $Na_2[Cu\{OCH(CF_3)_2\}_4]$,[39] $Na_3Y[\{\mu_2\text{-}OCH(CF_3)_2\}\text{-}(THF)_3]_6$,[40] $Na_2Y[\{\mu_2\text{-}OC(CH_3)(CF_3)_2\}_4\{OC(CH_3)(CF_3)_2\}\text{-}(THF)_3]$,[40] and $[Na\{\mu_3\text{-}OC(CF_3)_3\}]_4$.[38]

The motivation for the syntheses of these complexes was initially the development of new precursors for chemical vapor deposition (CVD) since it had been anticipated that the deposition of these alkoxides from the gas phase would lead to metal oxide films. However, it was soon realized that often metal fluorides were deposited instead. This was viewed as an indication of close CF···metal contacts in the gas phase which open up a kinetic route to the formation of metal fluorides. This hypothesis was further supported by the observation that in all of the above mentioned crystal structures, numerous intra- and intermolecular CF···metal contacts to each sodium ion exist. To illustrate this, two typical examples of metal environments in such fluoroalkoxides are given: the $Na(O_3F_5)$ coordination sphere in Na_2Y-hexafluoro-*tert*-butyl alcoholate [Na–O = 223.8(9), 226.9(7), 231.6(7) pm; CF···Na = 248.6(11), 251.4(8), 275.1(8) pm] and the $Na(O_2F_5)$ coordination sphere in Na_2Cu-hexafluoroisopropyl alcoholate [Na–O = 228.1(5), 231.8(5) pm; CF···Na = 248.1(6), 248.7(6), 259.0(6), 262.1(6), 279.1(6) pm].[39]

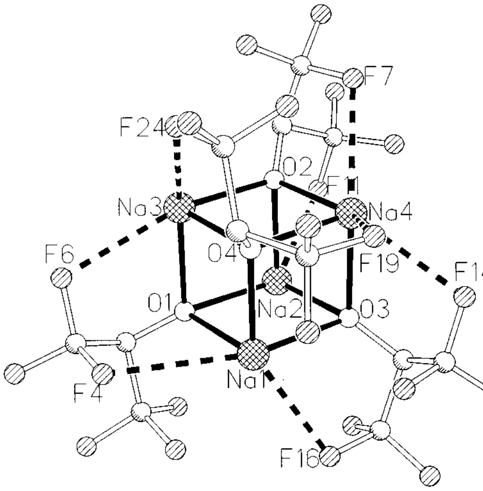

Figure 6. Crystal structure of HAGYAP (hydrogen atoms omitted), only intra-molecular CF···Na^+ contacts displayed.

Caulton et al. were also interested in finding out whether a higher degree of fluorination in metal alkoxides really leads to a significant increase in the volatility of the metal fluoroalkoxides. This has been stated many times in the literature, but as pointed out in the Caulton paper,[38] evidence for this is quite weak and therefore comparative experiments were performed. While it was demonstrated that the volatility in the series $Zr(O\text{-}^tBu)_4$ to $Zr(O\text{-}R_F)_4$ [R_F = $C(CH_3)_2(CF_3)$, $CH(CF_3)_2$, $C(CH_3)(CF_3)_2$, $C(CF_3)_3$] is almost unchanged, the TGA analysis of the tetrameric, cube-like $[NaOR_F]_4$ compounds showed that higher fluorination leads to an increased volatility.

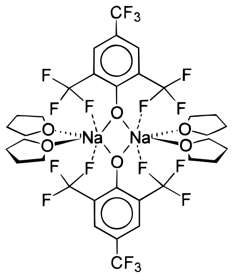

Figure 7. SISHUX.

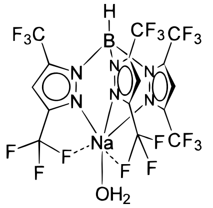

Figure 8. ZUVQOW.

A possible explanation for this effect has to take into account the numerous CF$\cdots$Na$^+$ interactions found in these complexes. Accordingly it was suggested by Caulton that the intramolecular CF$\cdots$Na$^+$ contacts observed in the solid state effectively shield the sodium center thereby preventing aggregation. This hypothesis is also in accord with greater shielding with an increasing degree of fluorination of the alcohols.[38]

^{23}Na magic angle spinning NMR spectroscopy and synchrotron X-ray powder diffraction have been used to study the binding of CF_2HCF_2H (HFC-134) in zeolite NaY.[41] The interaction of HFC-134 with the extraframework Na$^+$ is so strong that extraframework sodium cations in the sodalite cages migrate into the supercages hosting the hydrofluorocarbon as evidenced by a decrease in the ^{23}Na quadrupole coupling constant. Both ends of the HFC-134 molecules located within the supercages are bound to Na$^+$ and the CF$\cdots$Na$^+$ distances may be as short as 270 pm.

The highly toxic monofluoroacetate occurs in the leaves of *Dichapetalum cymosum* and has reportedly led to cattle poisoning.[42] The crystal structure of the sodium salt (NAFLAC20) was determined by Vedavathi and Vijayan and shown to display short CF$\cdots$Na$^+$ contacts.[43]

Short CF$\cdots$Na$^+$ contacts were also found in two interesting structures by Edelmann, Roesky et al. with bridging fluorinated phenoxy and benzenethiolato ligands.[44] The O-bridged salt $[\mu_2\text{-}\{2,4,6\text{-}(CF_3)_3C_6H_2O\}Na(THF)_2]_2$ (SISHUX) crystallizes as a dimeric species (Figure 7) with four short CF$\cdots$Na$^+$ contacts. The closely related S-bridged $[\mu_2\text{-}\{2,4,6\text{-}(CF_3)_3C_6H_2S\}Na(THF)_2]_x$ also has two short CF$\cdots$Na$^+$ per metal ion, but prefers a zigzag chain polymer structure in the crystal.

Dias et al. crystallized two sodium complexes with the polyfluorinated tris(pyrazolyl)borate ligand $[HB\{3,5\text{-}(C_2F_5)_2Pz\}_3Na(THF)]_2$[45] and $HB\{3,5\text{-}(CF_3)_2Pz\}_3Na(H_2O)$ (ZUVQOW)[46] (Figure 8) and observed short CF$\cdots$Na$^+$ contacts.

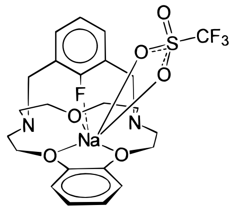

Figure 9. BenzoFN$_2$O$_3$·NaCF$_3$SO$_3$ (left) and FN$_2$O$_4$·NaCF$_3$SO$_3$ (right).

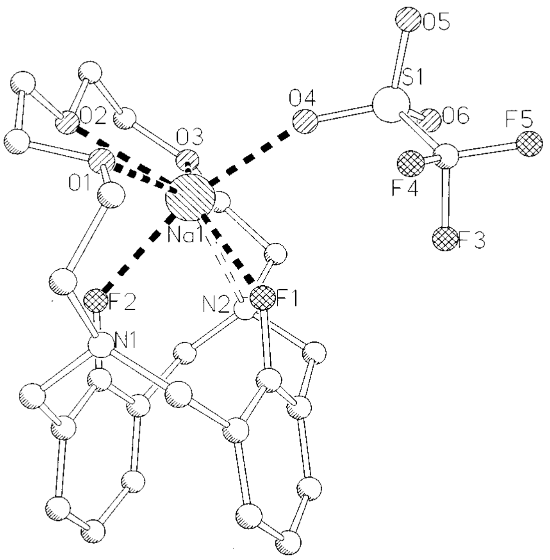

Figure 10. Crystal structure of F$_2$-[3.1.1]-cryptand·NaCF$_3$SO$_3$ (hydrogen atoms omitted).

Plenio and Diodone have synthesized and structurally characterized sodium complexes with the fluoro crown ethers FO$_5$ and the fluoro cryptands FN$_2$O$_3$, benzoFN$_2$O$_3$ (Figure 9, left), and FN$_2$O$_4$ (Figure 9, right) which display CF$\cdots$Na$^+$ contacts in the range of 237.5−267.1 pm.[12,47] The shortest CF$\cdots$Na$^+$ distances were observed in the crystal structure of F$_2$-[3.1.1]cryptand·NaCF$_3$SO$_3$ [229.8(3), 235.7(3) pm] and HF-[3.1.1]cryptand·NaClO$_4$ [236.0(4) pm] (Figure 10).[48]

All of the above-mentioned complexes of sodium with the fluoro macrocycles display close CF$\cdots$metal contacts in solution, which will be discussed in more detail in section III.H. Other structures with short CF$\cdots$Na$^+$ contacts are: $[Na_2(VO)(CF_3CO_2)_4(THF)_3(H_2O)]_2$,[49] Na-fluoropyruvate hydrate,[50] Na[*cis*-*mer*-Mo(C$_6$F$_5$)(CO)$_2$\{P(OMe)$_3$\}],[51] and $[Na\{W_2(OOCCCo_3(CO)_9)_2(OOCCF_3)_4(THF)_2\}]_2$.[52]

C. Potassium

Fluorocitrates are powerful inhibitors of aconitase, and the crystal structure of dipotassium 3−fluoro-3-deoxycitrate monohydrate was determined by Glusker et al.[53] to derive a model for the binding of fluorodeoxycitrate to the active site of the enzyme aconitase which may involve coordination of the CF unit to an iron center (refer to CF$\cdots$K$^+$ distances, Table 3).

The proposed environment of iron in this enzyme after coordination of the fluorocitrate is shown in Figure 11 (left). In accord with this drawing the idea of a CF unit coordinated to iron may be considered, since it helps to explain why aconitase can (irreversibly) cleave the stable CF bond and why this enzyme is so effectively inhibited by fluorocitrate.

Kawashima, Okazaki et al. have described four closely related structures of 1,2-oxastannetanide,[54]

Table 3. Short Formulas/Names of the Complexes (Pz = Pyrazolyl), CSD Refcodes, CF···K$^+$ Distances [pm], and Literature References[a]

formula/name	refcode	distance CF···K$^+$ [pm][a]	ref
KH-monofluoromalonate	BAWHAI	279.8	60
$K_2Ni[(OC_2(CF_3)_4O)_2]$	BIBSAG	300.7, 341.7	61
K-2,5-dihydro-2,2,5,5-$(CF_3)_4$-4-oxazolate	DENZOL	298.5, 298.8, 301.5	62
KH-3-fluoro-*o*-phthalate	FANWAS	331.5	63
K_2-3-fluoro-3-deoxycitrate	GABTAE	281.2, 284.6	53
$K[C(CF_3SO_2)_3]$	GEMNOB	298.6, 316.6	64
KH-difluorofumarate	KHDFMB	299.2(3), 321.3	65
KH-bis(trifluoroacetate)	KHFLAC	296.7, 333.7	66
$K[CF_3BF_3]$	KTFMFB	285.0(3), 287.5(3), 311.1(3), 331.8(3)	67
K_2-tetrafluorophthalate	KTFPHT	287.1(2), 287.9(2)	68
$[\mu_2\text{-}(2,4,6\text{-}(CF_3)_3C_6H_2O)K\text{-}(\mu_2\text{-THF})(THF)_2]_2$	SISJAF	286.7(3), 298.0(3), 321.8(3), 324.9(3)	44
$[\mu_3\text{-}(2,4,6\text{-}(CF_3)_3C_6H_2S)K(THF)]_x$	SISJIN	291.9(2), 294.5(2), 308.7(2), 309.4(2), 342.5	44
1,2-oxastannetanide	YAMYUG	306.1	54
1,2-oxagermetanide	YEMLEH	302(1), 328(2)	55
(K-18-crown-6)$(C_6F_5S)_3$Bi(NCS)	YULBEM	291.4	69
1,2-oxaboretanide	YUZLAG	314.6, 325.0, 344.8	57
1,2-oxagermetanide	ZEMVES	289.5(6), 333.1	56
$K[H_2B(3,5\text{-}(CF_3)_2Pz)_2]$	–	281.2(5), 285.9(4), 287.4(3), 321.5(4), 332.5(5)	58
$[K[HB(3,5\text{-}(CF_3)_2Pz)_3]\text{-}(MeCONMe_2)]_2$	–	282(1), 307(1), 311.1(6)	59

[a] Most C–F···K$^+$ angles are in the range of 100–130°.

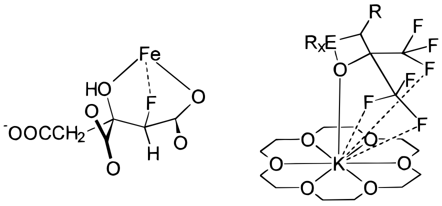

Figure 11.

1,2-oxagermetanide,[55,56] 1,2-oxaboretanide[57] complexes which are intermediates in the Peterson reaction (Figure 11, right, E = Sn, Ge). In all four structures there are between one and three RF_2C–F···K$^+$ contacts.

Edelmann, Roesky et al. showed that in the crystal the O-bridged salt $[\mu_2\text{-}\{2,4,6\text{-}(CF_3)_3C_6H_2O\}K(\mu_2\text{-THF})(THF)_2]_2$ exists as a dimeric species with four short CF···K$^+$ contacts and bridging fluorinated phenoxy and benzenethiolato ligands.[44] This structure is almost similar to that of the sodium salt (Figure 7) except for the two additional μ_2-THF. The closely related S-bridged $[\mu_3\text{-}\{2,4,6\text{-}(CF_3)_3C_6H_2S\}K\text{-}(THF)]_x$ prefers a ladder type chain polymer structure.

Dias et al.[58,59] described the crystal structures of the dimers $[\{H_2B(3,5\text{-}(CF_3)_2Pz)_2\}K]_2$ and $[\{HB(3,5\text{-}(CF_3)_2Pz)_3\}K\{\mu_2\text{-}(MeCONMe_2)\}]_2$ which are related to a sodium complex with the same ligand (Figure 8). Other crystal structures displaying short CF···K$^+$ contacts are: KH-monofluoromalonate hydrate,[60] $K_2Ni[(OC_2(CF_3)_4O)_2]$ tetrahydrate,[61] K-2,5-dihydro-2,2,5,5-$(CF_3)_4$-4-oxazolate-1,2-dimethoxyethane,[62] KH-3-fluoro-*o*-phthalate,[63] $K[C(CF_3SO_2)_3]$,[64] KH-difluorofumarate,[65] KH-bis(trifluoroacetate),[66] $K[CF_3BF_3]$,[67] K_2-tetrafluorophthalate,[68] and (K-18–crown-6)$(C_6F_5S)_3$-Bi(NCS).[69]

D. Rubidium

There is only a very small number of crystal structures which display short CF···Rb$^+$ contacts. Two of these have biological relevance: Fluorocitrate, whose rubidium–hydrogen–ammonium salt has CF···Rb$^+$ contacts of 297.9(5) and 309.5(4) pm (FLUCIT) is highly toxic due to the deactivation of aconitase.[70] Derivatives of the rubidium salt of 5-fluoroorotate monohydrate [CF···Rb$^+$ 288.0, 321.5 pm, RBFORM] are used in cancer treatment.[71] Fenton et al. synthesized Rb_2Na(hexafluoroacetylacetonate) [CF···Rb$^+$ 280–335 pm][72] and Davoy et al. prepared $Rb[(CF_3SO_2)_2CH]$ [CF···Rb$^+$ 326.3(3), 353.8(3) pm, RBMSME].[73]

E. Cesium

The coordination chemistry of cesium is much better explored than that of rubidium and consequently a much larger number of compounds with CF···Cs$^+$ contacts have been described (Table 4). Studies involving this metal ion are facilitated because ^{133}Cs is a sensitive, 100% abundance NMR nucleus.

Davidson, Lindsell et al. reported the synthesis of $CpM'(SC_6F_5)_4M$ (M′ = Mo, W; M = K$^+$, Rb$^+$, Cs$^+$) complexes in which M′ and M are bridged by four pentafluorobenzenethiolates (Figure 12, left)[74,75] or by tetrafluorobenzenethiolates.[76] Variable temperature ^{19}F NMR spectroscopic studies of $CpMo(SC_6F_5)_4$-Cs in toluene-*d*$_8$, CD_2Cl_2, and $(CD_3)_2CO$ between −80 and 40 °C revealed three different phenomena: reversible coordination of $CpMo(SC_6F_5)_4^-$ to Cs$^+$, fluxional motion involving the SC_6F_5 ligands and variable coupling constants of the ^{133}Cs, and ^{19}F nuclear spins. At low temperatures a $J(^{133}\text{Cs}-^{19}\text{F}) = 58$ Hz was detected in toluene solvent, with one of the respective ortho-fluorines of each SC_6F_5 ligand coupling to Cs$^+$. In the more polar solvent $(CD_3)_2CO$ coupling of ^{19}F and ^{133}Cs was not observed, which is probably due to the better solvation of Cs$^+$ by acetone. Basically the same dynamic behavior was found for the complexes of M = K$^+$ and Rb$^+$ with the same ligand.

The respective thallium complexes $CpM'(SC_6F_5)_4$-Tl and $CpM'(CO)_2(SC_6F_5)_2$Tl (Figure 12, M′ = Mo, M = Tl) display the same type of dynamic processes and at low temperatures a coupling between $^{19}\text{F}-^{203/205}\text{Tl}$ of 3537 Hz and 3770 Hz, respectively, was detected.[77] In addition both thallium complexes have been characterized by X-ray crystal structure analysis (FOFDUZ10, FOFFAH10) and found to display short

Table 4. Short Formulas/Names of the Complexes, CSD Refcodes, CF···Cs$^+$ Distances [pm], and Literature References[a]

formula/name	refcode	distance CF···Cs$^+$ [pm]	ref
CsAm(hfa)$_4$	CAMHFA	320(2), 328(2), 335.0(2)	84
CsEu(hfa)$_4$	CEUHFA	316(2), 318(2), 330(2)	84
CsH(bis(trifluoroacetate))	CHFLAC	329.9, 352.7, 366.9	66
Cs[(CF$_3$)$_2$BF$_2$]	CSFMFB	325.8(6), 333.0(7), 335.3(5), 338.5(4), 339.1(4), 368.2(6)	83
CsY(hfa)$_4$	CYSFAC	320.7(10), 326.5(14), 331(2), 375(2)	85
Cs(F$_3$CO)	KIMLEX	309.3, 309.5, 316.0, 318.0, 323.7, 338.8, 339.7, 359.2, 360.8	87
Cs(CF$_2$(SF$_3$)$_2$F)	PAFTOF	326.8	82
Cs(1-(2-thienyl)-4,4,4-trifluorobutane-1,3-dione)	TFBUCS	327(2), 343(2), 348(2)	86
c-F$_4$N$_4$O$_4$·CsCF$_3$SO$_3$	–	284.3(3), 304.7(3), 308.2(2), 337.2(2)	79

[a] Most C–F···Cs$^+$ angles are in the range 90–140°.

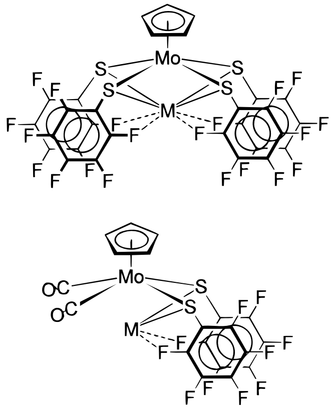

Figure 12.

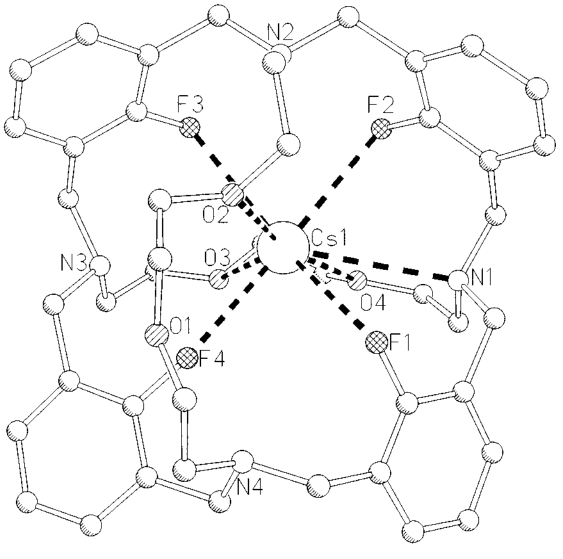

Figure 13. Crystal structure of c-F$_4$N$_4$O$_4$·CsCF$_3$SO$_3$ (hydrogen atoms and triflate omitted).

CF···Tl$^+$ distances [297.8(1)–319.7(1) pm and 309.0(9)–326.5(10) pm] (see also section VI.B.).[78]

Plenio and Diodone prepared the macropolycyclic ligand c-F$_4$N$_4$O$_4$ which has four potential CF donor sites and is able to encapsulate large metal ions within its cavity (Figure 13).[79] In the crystal structure of c-F$_4$N$_4$O$_4$·Cs$^+$CF$_3$SO$_3$$^-$ the metal ion has a F$_4$O$_3$N$_1$ coordination sphere in which three of the four shortest contacts to cesium are made by fluorine atoms [Cs–O 305.4(3), 311.0(3), 322.2(3) pm, Cs–N 344.6(4) pm, CF···Cs$^+$ 284.3(3), 304.7(3), 308.2(2), 337.3(3) pm]. To assess the contribution s_i of each donor atom or each type of donor atoms in the coordination sphere of cesium in c-F$_4$N$_4$O$_4$·Cs$^+$CF$_3$SO$_3$$^-$, the valence bond sum $S = \sum s_i$, i.e., the individual values of s_i for the nine donor atoms close to cesium were calculated according to the method by Shannon and Brown.[80] In the cesium complex the four CF units from the ligand contribute $s_F = 0.20 + 0.127 + 0.118 + 0.065 = 0.51$, the three ether units $s_O = 0.17 + 0.151 + 0.119 = 0.44$, and the nitrogen atom an estimated $s_N = 0.08$ which all add up to $S = \sum s_i = 1.03$, being close to the ideal value of $S = 1$.[81] In conclusion the CF units in this complex are more important for the coordination of cesium than the ether oxygen atoms.

In the crystal structure of Cs$^+$(CF$_2$(SF$_3$)$_2$F$^-$) reported by Mews et al. the cesium ion is surrounded by 12 fluorine atoms [297.6(2)–339.1(2) pm] of which 10 are bonded to sulfur while only two long contacts are made by CF units.[82] In Cs[(CF$_3$)$_2$BF$_2$] described by Bürger et al.[83] cesium makes 12 contacts with F atoms which are shorter than 368 pm; of these the shortest four [304.8(3), 304.8(3), 321.6(8), 321.6(8) pm] are with BF units, while five of the remaining eight are CF···Cs$^+$ interactions. Other crystal structures displaying short CF···Cs$^+$ contacts are: CsAm(hfa)$_4$ (hfa = hexafluoroacetylacetonate) and CsEu(hfa)$_4$,[84] CsH(bis(trifluoroacetate)),[66] CsY(hfa)$_4$,[85] Cs(1-(2–thienyl)-4,4,4-trifluorobutane-1,3-dione),[86] and Cs(F$_3$CO).[87]

F. Distribution Statistics of the CF···Metal Distances

For three alkali metal ions a sufficient number of CF···metal distances from crystal structure determinations are available for a statistical evaluation of the bond length distribution. The usefulness of such an approach for the verification of attractive interatomic contacts has been validated by the identification of very weak interactions such as CH···O hydrogen bonds.[88]

In the following figures the frequencies of fluorine–metal distances are plotted in intervals of 10 pm (Na$^+$ Figure 14, K$^+$ Figure 15, Cs$^+$ Figure 16). A first distinct feature of these histograms is broad but clearly visible maxima in the distributions of the metal–fluorine distances. For CF···Na$^+$ contacts this maximum is between 255 and 275 pm, while the number of observed metal–fluorine contacts to the shorter as well as to the longer side is much smaller. In the case of the K$^+$ complexes the maximum occurs between 285 and 305 pm and the number of observed contacts slowly tails off toward longer CF···K$^+$ distances. For the Cs$^+$ complexes the number of available data is rather small, but even here a clear

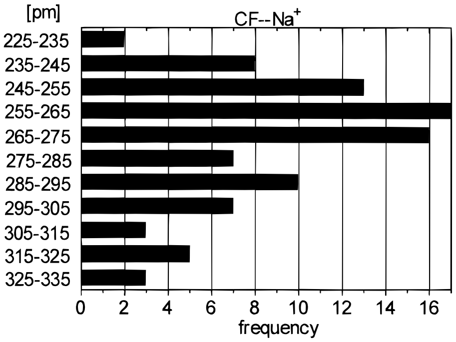

Figure 14. Histogram of observed CF···Na^+ contacts plotted in intervals of 10 pm.

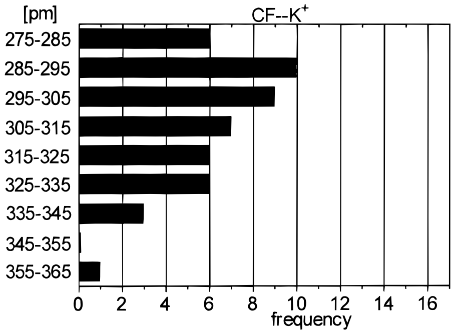

Figure 15. Histogram of observed CF···K^+ contacts plotted in intervals of 10 pm.

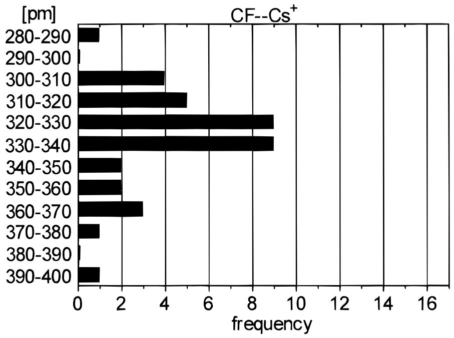

Figure 16. Histogram of observed CF···Cs^+ contacts plotted in intervals of 10 pm.

maximum between 320 and 340 pm is visible. The message from these data is clear. The interaction between covalently bonded fluorine and the metal ions is attractive and the observed metal—fluorine distances are indicative of a preferred metal—fluorine bond length.

The analysis of the bond length data can also help to determine whether a useful selection of the threshold values for the CSD search was made. In this respect note that the upper limits chosen for Na^+, K^+, and Cs^+ complexes encompass the large majority of CF···metal distances found.

G. Calcium, Strontium, and Barium

The discovery of high-T_C superconducting materials has fueled research into volatile barium compounds for the CVD generation of superconducting thin films. Consequently a number of volatile barium complexes with hfa or hexafluoro-*tert*-butanolate have been synthesized. In the crystal structures of these complexes several short CF···Ba^{2+} contacts are observed: $BaCu_2[OC(CH_3)(CF_3)_2]_6$,[89] has a $Ba(O_4F_8)$ coordination sphere [294.4(10), 295.8(10), 310.2(10), 314.2(10) pm, KIWZIZ], polymeric $[Ba(hfa)_2(H_2O)_2]_x$ [292(2), 297(2) pm, KOWPOB];[90] polymeric $[Ba(hfa)_2(Et_2O)]_x$ [276, 297, 309 pm, WEDGAN];[91] $(H_3NC_2H_4NH_3)_{1.5}Ba(hfa)_5{\cdot}EtOH$ [328.7(8) pm, PINCUK];[92] $Ba_5[(\mu_5\text{-}OH)\{\mu_3\text{-}OCH(CF_3)_2\}_4\{\mu_2\text{-}OCH(CF_3)_2\}_4\{OCH(CF_3)_2\}(H_2O)(THF)_4]$ [299(2) pm][93] and BaY_2[(di-*tert*-butylacetylacetonate)$\{\mu_2\text{-}OCH(CF_3)_2\}]_4$ [290.5, 294.5, 303.3, 304.6, 307.2, 311.2, 311.3, 315.6 pm, WEBNAS],[94] $Ba_4[(\mu_4$-pivaloyltrifluoroacetonato$)_2(\mu_2$-pivaloyltrifluoroacetonato$)_6]$ [287.4, 291.6, 299.5 pm, TAZCAY][95] and $Ba_3[\mu_2$-1,1,1,5,5,5-hexafluoro-4-(phenylamido)pentan-2-olato$]_6$ [304.5, 304.8, 311.7 pm, NACPIQ].[96] The only X-ray crystal structure with short CF···Ca^{2+} contacts is $[Ca(hfa)(H_2O)_2]_2$ [252.4(5) pm, KOMPIV]. [90]

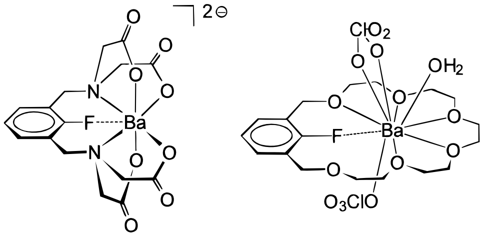

Figure 17. $[FXDTA{\cdot}Ba]^{2-}$ (left) and $FO_6{\cdot}Ba(ClO_4)_2$ (right).

Fluoroxylene-diamino tetraacetate (fxdta) is a relative of the well-known complexon edta[97] and complexes of the fluorine-containing ligand with alkaline earth metal ions display CF···metal contacts in aqueous solution (Figure 17 left, proposed structure of the Ba^{2+} complex). This is evidenced by characteristic shifts of their ^{19}F NMR resonances of up to 4.8 ppm, relative to the ^{19}F NMR signals of the tetrasodium salt of fxdta. In a NMR-competition experiment it was also shown that fxdta forms more stable complexes than hxdta. This is indicative of a stabilizing effect of CF coordination since the only difference between hxdta and fxdta is that the former ligand has a CH instead of a CF unit. Short CF···Ba^{2+} distances were also observed in barium complexes of fluoro crown ethers: $FO_5{\cdot}Ba(ClO_4)_2$ 279.9(8) pm and in $FO_6{\cdot}Ba(ClO_4)_2$ (Figure 17, right) 299.0(3) pm.[47,98]

Related complexes of group I and group II metal ions with other halocarbons (X = Cl, Br, I) which display short CX···metal contacts are less common.[99,100,101]

H. Complexes of the Fluoro Macrocycles in Solution

The fluoro macrocycles by Plenio et al., of which examples are shown in Figures 5, 9, 10, 13, 17, and 19, are unique with respect to CF···metal contacts, because they were the first neutral ligands to form stable complexes with alkali and alkaline earth metal ions in solution and because the nature of the CF···metal contacts could be probed with a variety of techniques.[12,47,48,79,98,102] Such interactions only seem to be possible when the overall content of fluorine in the macrocycle is low. In contrast perfluorinated crown ethers and cryptands do not coordinate metal ions at all as shown by Lagow et al.[103] (Figure 18) and Farnham and co-workers.[104]

The reason for this is the electron-withdrawing effect of CF_2 units, which effectively destroys the

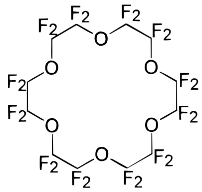

Figure 18.

donor ability of the oxygen atoms; conversely, the CF_2 units themselves are not preorganized to encapsulate metal ions. Obviously, the formation of CF···metal contacts requires an efficient spatial organization of the donor units.[105,106] This condition is met in the fluoro macrocycles derived from 1,3-bis(bromomethyl)-2-fluorobenzene and in the following paragraphs some of the remarkable properties of complexes with these ligands will be described.

Proof in favor of CF···metal contacts in solution is difficult to obtain but this should not be confused with the perception of an inherent weakness of such interactions. Quite in contrast it rather reflects our lack of knowledge about the processes occurring in solution and at the same time underestimates the dynamics involved. To obtain a more realistic picture of the situation as it is, one should rather ask which spectroscopic techniques are available and have been utilized for the observation of close CF···metal contacts in solution. After evaluating the literature on such interactions the results are sobering, since virtually the only tool which has been used with some success is NMR spectroscopy. Firm evidence in favor of close CF···metal contacts in solution was obtained by observing coupling constants between ^{19}F and a metal nucleus by NMR spectroscopy in complexes with the following metals: $^{6,7}Li$, ^{89}Y, $^{107,109}Ag$, ^{133}Cs, and $^{203,205}Tl$. Another sign indicative of close CF···metal interactions is available from ^{19}F NMR spectroscopy, for upon addition of metal salts to the fluoro macrocycles the ^{19}F NMR signals are significantly shifted by between $+10$ and -30 ppm relative to the signal of the free fluoro macrocycle. This leads to very characteristic ^{19}F NMR signals for each metal complex; however, caution is advisable with respect to the correlation of the ^{19}F NMR shifts with the degree of CF···metal interaction, since the origin of ^{19}F NMR shifts is not entirely understood.[107]

More reliable for the detection of CF···metal contacts are the $^{1}J(^{13}C-^{19}F)$ coupling constants,[108] which seem to be correlated with the strength of this interaction. This can be easily explained: In the metal complexes of fluoro macrocycles the metal ions coordinated within the cavity compete with the phenyl ring for fluorine lone pair electron density. The metal ion will only compete successfully when it is efficiently coordinated by a CF unit within the macrocyclic cavity as this leads to a withdrawal of lone pair electron density from the CF bond, which is accompanied by a decrease of the $^{1}J(CF)$ coupling constant.

The effect of the CF donor units on the stability of the alkali metal complexes can also be determined, when the coordination properties of the fluoro macrocycles are compared with those of reference systems, which differ from the former ligands only with respect to the single fluorine which was replaced by a hydrogen atom. Three important examples of such closely related pairs of macrocycles are depicted in Figure 19.

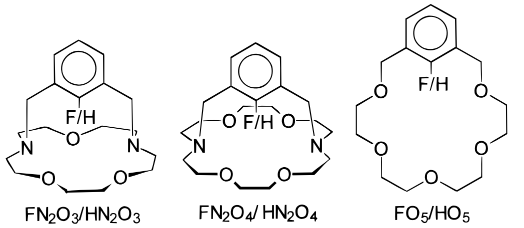

Figure 19. Pairs of fluorinated and fluorine-free macrocycles.

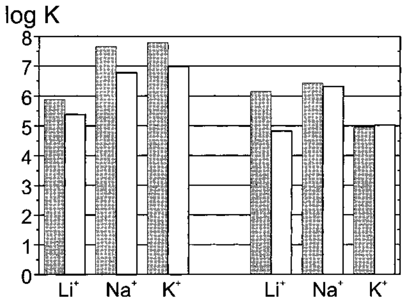

Figure 20. Stability constants (log K) of the complexes of FN_2O_3, HN_2O_3 (right) and FN_2O_4, HN_2O_4 (left) with Li^+, Na^+, and K^+ as determined in picrate extraction experiments (shaded bars are fluoro cryptands, colorless bars are F-free cryptands).

A comparison of the stability constants of complexes of fluoro macrocycles with those of the fluorine-free macrocycles (Figure 20), reveals that the fluorine-containing cryptands form more stable complexes than the corresponding fluorine-free cryptands in most cases, but not as a general rule.

A stabilization of the complexes of the fluorine-containing macrocycles with respect to those of the fluorine-free macrocycles is only observed when the metal ion is small enough to be able to migrate into the cavity of the macrocycle to contact fluorine, which is located in the interior of the cavity. This is easily possible for Li^+ in its complex with FN_2O_3, whereas Na^+ and K^+ are too big. However, in the case of FN_2O_4 which has a larger cavity, even the larger metal ions Na^+ and K^+ can profit from the stabilization by the CF units.

It can thus be stated that the significant differences in the stabilities of group I and II metal ion complexes with fluorine-containing and fluorine-free macrocycles are primarily due to stabilizing CF···metal interactions.

I. Stereoselective Synthesis Using CF Donors as Directing Groups

The stabilization of transition states via coordination of covalently bonded fluorine to lithium, magnesium, and aluminum cations may be responsible for the unexpected stereochemical outcome of a number of organic transformations. This was suggested by some authors and this hypothesis is, in some cases, backed by theoretical studies.

Ishikawa et al. for example investigated nucleophilic reactions of F-2-methyl-2-pentene(E)-F-4-methyl-2-pentene with organomagnesium and -lithium reagents leading to α- and γ-fluorine elimination. The reaction mechanism of the γ-elimination was

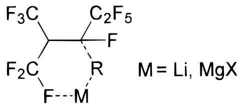

Figure 21.

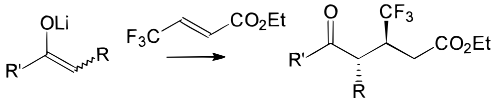

Figure 22.

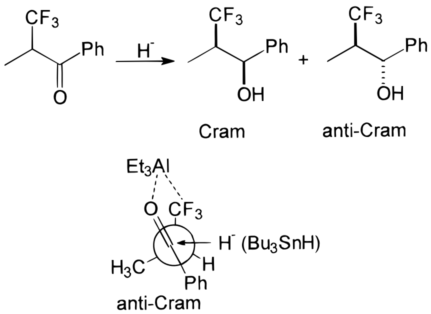

Figure 23.

explained with the formation of a six-membered chelating ring involving CF$\cdots$Mg^{2+} or CF$\cdots$Li$^+$ coordination (Figure 21).[109]

Kitazume, Yamazaki, et al. investigated the Michael addition of lithium enolates to ethyl 3-(trifluoromethyl)acrylate (Figure 22) which proceeds with high diastereoselectivity.[110] The importance of CF$\cdots$Li$^+$ contacts for the proposed mechanism was suggested, based on the distribution of the products and further supported by ab-initio calculations.[111,112]

Attractive CF$\cdots$Li interactions were also postulated to be important in other Michael type addition reactions.[113] Morizawa et al. reported that the transformation of the lithium enolate prepared from ethyl 3-methyl-4,4,4-trifluorobutyrate with MoO$_5$–pyridine–HMPA complex provides predominantly ethyl (2*S**,3*S**)-2-hydroxy-3-ethyl-4,4,4-trifluorobutyrate and that the NaBH$_4$ reduction of the corresponding 2-oxobutyrate preferentially affords (2*R**,3*S**)-hydroxyester. In both reactions CF$\cdots$Li$^+$ or CF$\cdots$Na$^+$ interactions were made responsible for the high degree of stereocontrol.[114]

A remarkable stereoselectivity for the anti-Cram reduction of 2-(trifluoromethyl)propiophenone was observed by Fuchikami and Hanamoto in the presence of added Lewis acid and it was suggested that CF$\cdots$Al interactions with the –CF$_3$ group were responsible for this selectivity (Figure 23).[115]

A CF$\cdots$Al interaction was postulated by Kuroboshi and Ishihara to account for the diastereoselective reduction of α,α-difluoro β-hydroxy ketones with diisobutylaluminum hydride.[116] Wong and Paddon-Row performed ab-initio calculations on the addition of LiH to fluoroethanal and 2-fluoropropanal. The results of their study confirmed that in the most stable transition structure for each system electrostatic interactions between lithium and fluorine dominate.[117] Qian and Nakai attributed the stereoselective F-enolate formation to stabilizing CF$\cdots$Li interactions.[118] Koga et al. discovered that chiral chelated lithium amides having a fluorine-containing alkyl group on the amide nitrogen induce a high enantioselectivity in the kinetic deprotonation of 4-substituted cyclohexanones, which might be rationalized by postulating lithium–fluorine contacts.[119] CF$\cdots$Li interactions may also be important during the addition of lithium amides to (trifluoromethyl)-styrene.[120]

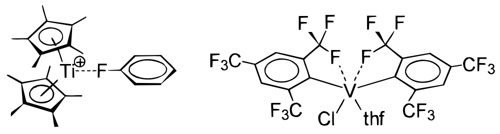

Figure 24.

In two studies Schleyer et al.[121] and Saa et al.[122] used ab-initio and MNDO calculations to explore the origin of ortho-lithiation in donor substituted aromatic compounds; in both calculations the ortho-lithiation of fluorobenzenes was favored due to CF$\cdots$Li coordination. Schleyer also demonstrated that the reaction energy of the ortho-lithiation of fluorobenzene is 13.5 kcal/mol more favorable than that of para-lithiation. Clark and v. Onciul performed UMP4/6–31G*//6–31G* calculations on the complexation of Li$^+$ to the β-fluoro- or β-chloroethyl radicals to Li$^+$ which produce cation affinities of the fluoro radicals of around 40 kcal/mol, while those of closed-shell species C$_2$H$_5$F are slightly lower.[123] Schleyer, Streitwieser et al. did calculations on the complexes of LiF and CH$_3$F which at the 6-31+G* level led to a stable minimum for the linear C_{3v} symmetry H$_3$CF$\cdots$LiF structure.[124]

IV. Complexes of the Transition Metals Including Zn, Cd, Hg

With the exception of zirconium and silver complexes, crystallographic or spectroscopic evidence in favor of CF$\cdots$metal interactions within the transition metal series is limited to very few examples. In addition, a number of compounds display long and possibly nonbonded contacts below the threshold value set for our search. In the case of the transition metals neither a van der Waals derived threshold nor a purely ionic approach appear very helpful. To address these problems basically every single metal complex would require an individual evaluation of its coordination sphere. Such an approach poses the danger of being biased and the simple application of a reasonable overall threshold for the first (CF$\cdots$metal $<$ 270 pm) and the second and third transition series (CF$\cdots$metal $<$ 300 pm), which is always shorter than the combined van der Waals radii, was preferred.

A. First Row Transition Elements Sc–Zn

In the first transition series there are basically only two complexes in which convincing evidence in favor of significant CF$\cdots$M interactions is available. Teuben and co-workers determined the X-ray crystal structure of [(Cp*)$_2$Ti(FC$_6$H$_5$)][BPh$_4$] (Figure 24, left) which displays an extremely short CF$\cdots$Ti distance of 215.1(2) pm.[125] This complex is unstable in solution and decomposes to yield the CF activated product [{(Cp*)$_2$Ti}$_2$(μ_2-F)$_2$]. The other example is a vanadium complex by Gibson et al.[126] and in VCl{2,4,6-(CF$_3$)$_3$C$_6$H$_2$}$_2$(THF) two short CF$\cdots$V interactions [230.6(2), 237.8(2) pm] contribute to an overall pseudo-

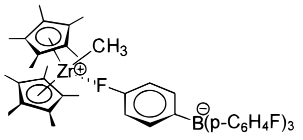

Figure 25.

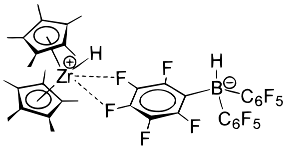

Figure 26. VUTHOH01.

octahedral $V(C_2OClF_2)$ coordination sphere (Figure 24, right), while in the related complex $V\{2,4,6-(CF_3)_3C_6H_2\}_2OLi(THF)_3$ only one long contact exists [CF···V 266.8(4) pm].

Other examples of complexes with weak CF···metal interactions are $Co\{HB(3,5-Me_2Pz)_3\}(C_6F_5)$ [CF···Co 265(2) pm, PFTPCO];[127] $Zn\{2,4,6-(CF_3)_3C_6H_2\}_2$, [CF···Zn 253.2(6), 254.4(6), 256.1(6), 260.9(6), 273.3(6) pm, VOTGAM];[128] $Zn_2\{N(SiMe_3)_2\}[S\{2,4,6-(CF_3)_3-C_6H_2\}]_3$ [CF···Zn 269.5(4) pm, PAMWOP];[129] Zn-(5,10,15,20-$(C_6F_5)_4$-porphyrinato) [CF···Zn 265.2 pm, ZALJIG].[130]

B. Second Row Transition Elements Y−Cd

1. Zirconium

The reaction of zirconocene dichlorides with the Lewis-acidic cocatalyst methylalumoxane (MAO) generates zirconocenium cations, which are believed to be the catalytically active species in the Ziegler−Natta polymerization of olefins.[131] The large excess (100−1000-fold) in which the alumoxane cocatalyst is needed currently represents one of the major drawbacks for the commercialization of homogeneous olefin polymerization with these catalysts.[132] An alternative activation process involves the use of $B(C_6F_5)_4^-$ (or related borates) for the stabilization of the metallocene cation. In recent years more and more evidence has been accumulating which proves that the CF units of the borate take part in the coordination of the cationic metal center and it is believed that this interaction has a pronounced influence on the polymerization behavior of such catalytic systems.

The first evidence for an interaction between CF units of $B(p\text{-}C_6H_4F)_4^-$ and a cationic zirconocene came from work by Horton and Orpen,[133] who noticed that at low temperatures the ^{19}F NMR spectra of $(Cp^*)_2ZrMe^+B(p\text{-}C_6H_4F)_4$- and related compounds display two types of magnetically distinct fluorine atoms in a 3:1 ratio. The coordination of a single fluorine to $(Cp^*)_2ZrMe^+$ (Figure 25) was suggested since one ^{19}F NMR resonance is shifted to higher field (with respect to the three other fluorine) by more than 50 ppm.

Crystallographic evidence for such an interaction was found by Marks et al. in the complex $(Cp^*)_2ZrH^+\ HB(C_6F_5)_3^-$, [CF···Zr 241.6(3), 253.4(3) pm, VUTHOH01, Figure 26].[134] Even though the CF···Zr interactions were described as fairly weak, there is a small elongation of the corresponding C−F bonds.

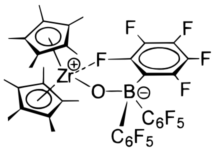

Figure 27. LAMXIG.

The preference of CF···Zr versus BH···Zr interactions seemed surprising but was attributed to steric constraints which appear to prevent the close approach of the BH group.

To probe the influence of counter ion coordination to the highly electrophilic cationic zirconium center, the complexes of four different anions (sorted according to their coordinating abilities) $MeB(C_6F_5)_3^- > B(C_6F_4SiMe_2tBu)_4^- \approx B(C_6F_4Si^iPr_3)_4^- > B(C_6F_5)_4^-$ were investigated.[135] Although the first anion is coordinated to the metal via the methyl group the other three anions display CF···Zr contacts in solution as evidenced by ^{19}F NMR spectroscopy. In the case of the most weakly coordinating counter ion $B(C_6F_5)_4^-$ even solvent molecules such as toluene compete with the anion for coordination to zirconium when the metal center is sterically accessible. This seems to be the case in the geometrically constrained cation $[(Me_4Cp)SiMe_2(N^tBu)]ZrMe^+$. It is very interesting to learn that the polymerization activity of the cationic zirconocenes is ranked according to the coordinating ability of the counter ion, reaching a maximum with the most weakly coordinated anion and the sterically most accessible zirconium center. From a viewpoint of chemical stability $B(C_6F_4SiMe_2tBu)_4^-$ and $B(C_6F_4Si^iPr_3)_4$ anions are preferred, since catalytically active systems with $B(C_6F_5)_4^-$ decompose much faster. However, at elevated temperatures reactions of the former two anions with cationic zirconium complexes also result in formation of zirconocene fluorides.[135]

The reaction of $(Cp^*)_2ZrMe_2$ with $[Et_3NH][(C_6F_5)_3BOH]$ was reported by Siedle et al. to yield $(Cp^*)_2ZrOB(C_6F_5)_3$ (Figure 27).[136] In the crystal the borate is bonded to zirconium forming a six-membered chelating ring via Zr−O [191.2(3) pm] and CF···Zr bonds [234.6(3) pm, LAMXIG]. In the ^{19}F NMR spectra recorded below −75 °C the resonance of one fluorine is shifted by over 50 ppm from the region typical of ortho-F in BC_6F_5 rings to −190.3 ppm and was assigned as being bonded to the metal. The dynamic behavior of the C_6F_5 rings was investigated by temperature variable ^{19}F NMR spectroscopy and the evaluation of the ^{19}F DNMR data yielded $\Delta G^\# = 10 \pm 0.5$ kcal/mol for the concomitant interconversion of all C_6F_5 rings. Consequently the authors suggested that cleavage of the CF···Zr bond is the primary contributor to this energy barrier.

Research by Erker et al. is directed toward using cationic zirconocenes as catalytic reagents for C−C bond formation as well as for improved polymerization catalysts. One line of research followed in this respect is to covalently link the fluorinated borate counteranion to the metallocene catalyst.[137] The synthesis of such zirconium−boron betaine complexes (Figure 28) can result in compounds in which a CF unit is coordinated to the cationic zirconium center. However, to be catalytically active the facile opening

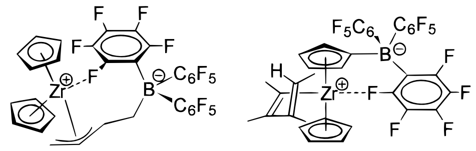

Figure 28.

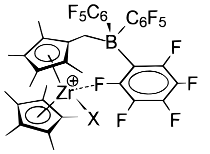

Figure 29.

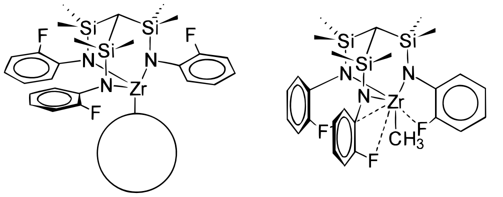

Figure 30. The behavior of "active ligands" with respect to the coordination of zirconium, depending on the steric bulk of additional ligands coordinated to this metal.

of this CF···Zr (CF···Hf) chelate has to occur readily, whereas reclosing it after the reaction of one monomer would allow the system to rest at the stage of mono-insertion. The exertion of such a degree of control over the reactivity of the metal center via reversible coordination of a CF unit is a typical feature of hemilabile ligands.[138] The identification of close CF···Zr interactions in betaine complexes rests on X-ray crystal structures analyses by which relatively short CF···Zr contacts [242.3(3) pm, 140.0°, Figure 28 left][137] [232.2(2) pm, 150.6°, Figure 28 right][139] were found. In ^{19}F NMR investigations basically the same features as described above (pronounced shielding of the ortho-F signal and dynamic behavior) were observed.[137]

Piers and co-workers recently reported several X-ray crystal structures of new zirconocenes with short CF···Zr interactions [Figure 29, X = Cl 226.7(5) pm, X = H 241.4(3) pm, X = C_6H_5 223.7(4) pm]. Once again the hemilabile nature of the CF donor units was evidenced by the facile decoordination of the pentafluorophenyl group.[140]

The use of hemilabile CF donor units—in a chemically very different environment—was described by Gade et al.[141] for different tripodal ligands containing an "active ligand" periphery. According to the authors active means that depending on the steric and electronic situation of the metal center, the peripheral CF units may or may not participate in the bonding of the metal. In the $Zr-CH_3$ complex depicted in Figure 30 the active involvement of the peripheral CF donors in solution appears likely since $^{19}F-^{13}C$ and $^{19}F-^{1}H$ NMR coupling to the $ZrCH_3$ group was observed. Short CF···Zr interactions were found in the crystal structures of $\{(2\text{-}FC_6H_4NSiMe_2)_3\text{-}CH\}Zr(\mu\text{-}Cl)_2Li(OEt_2)_2$ [CF···Zr 253.5(5) pm, ZAXFAF] and that of the almost identical complex $\{(2\text{-}FC_6H_4NSiMe_2)_3SiMe\}Zr(\mu\text{-}Cl)_2Li(OEt_2)_2$, ZOJKUE] with a SiMe bridgehead instead of a CH group [CF···Zr 251.1(2) pm].[142] CF···Zr distances in the related complexes $HC(SiMe_2N(2\text{-}FC_6H_4))_3Zr(S_2C)Fe(CO)_2(\eta^5\text{-}C_5H_5)$ and $HC(SiMe_2N(2\text{-}FC_6H_4))_3Zr(SCN\text{-}Ph)Fe(CO)_2(\eta^5\text{-}C_5H_5)$ are 256.3(8) and 270(1) pm, respectively.[143]

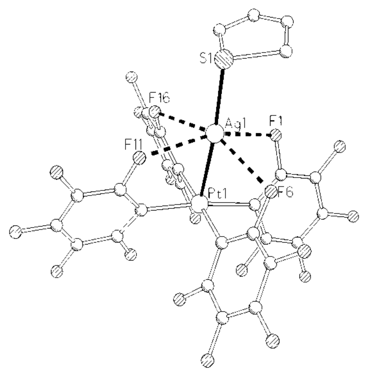

Figure 31. Crystal structure of KOCPIB (hydrogen atoms omitted).

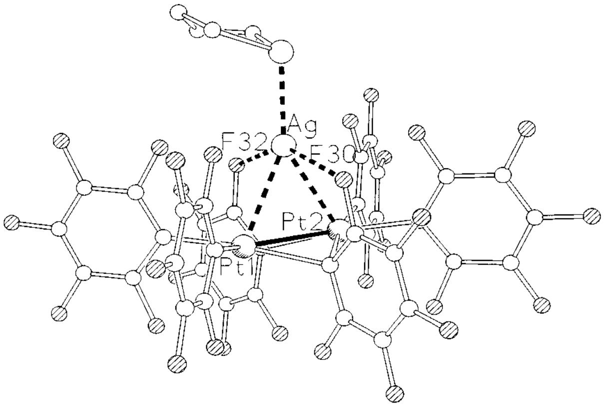

Figure 32. Crystal structure of the $AgPt_2$ cluster (hydrogen atoms omitted).

2. Silver

The coordination chemistry of the silver(I) d^{10} cation is characterized by the absence of crystal field effects and is therefore remotely related to that of the alkali metals, even though Ag^+ is classified as relatively soft.

A large number of platinum−silver−C_6F_5 clusters displaying short CF···Ag contacts have been described by Uson, Forniés, and co-workers from Zaragoza University, whose work has also been reviewed.[144] Two complexes which are representative examples of their investigations are shown in Figure 31[145] and Figure 32.[146] All other complexes from these authors are closely related with respect to CF···Ag interactions: CEVZIM,[147] CUXWAT,[148] CUXWEX,[149] FORCOE,[150] JEVLOL,[151] KOCPIB, KOCPEX, KOCPOH,[145] SUJJEM,[152] WEDTEE,[153] YOZWOZ,[154] ZEKMIL,[155] ZUYPAK,[156] and $[(C_6F_5)_2Pt(\mu\text{-}OH)\{\mu\text{-}(Ph_2P)_2CH_2\}\{Ag(PPh_3)\}Pt(C_6F_5)_2]\cdot(5\ C_7H_8)$[157] (CF···Ag distances Table 5).

In all of the above-mentioned clusters the pentafluorophenyl groups bonded to platinum act as bridging ligands, with the C-terminus bonded to platinum and the CF units forming short contacts to silver (Table 5). Depending on the number of C_6F_5 groups, up to eight CF···metal contacts may exist in one complex (for an example with Tl^+ see Figure 40). The first example of a coupling of $^{107,109}Ag$ and ^{19}F nuclear spins (J = 60 Hz) in such $Pt-Ag-C_6F_5$ clusters was reported only recently by Forniés et al.

Table 5. Short Formulas of the Complexes (tht = SC_4H_8), CSD Refcodes, CF···Ag^+ Distances [pm], and Literature References[a]

formula	refcode	distance CF···Ag^+ [pm]	ref
$[Pt_2Ag_2Cl_4(C_6F_5)_4]^{2-}$	CEVZIM	260.2(10), 269.6(10)	147
$(C_6F_5)_3(tht)PtAg(PPh_3)$	CUXWAT	275.7(7). 276.3(8), 279.1(7)	148
$[Pt_2Ag(\mu\text{-}C_6F_5)_2(C_6F_5)_4OEt_2]^{2-}$	CUXWEX	265.4(10), 267.0(10), 287.1(11), 290.8(11)	149
$[Pt_2AgCl_2(C_6F_5)_4OEt_2]^{2-}$	FORCOE	285(1)	150
$[PtCl_2\{(\mu\text{-tht})(C_6F_5)_3PtAg(\eta^2\text{-toluene})\}]$	JEVLOL	286.6(11), 273.2(9), 273.3(9)	151
$[(tht)(C_6Cl_5)(C_6F_5)_2PtAg(PPh_3)]$	KOCPEX	275.9(14), 292.4(13)	145
$[(C_6F_5)_4PtAg(tht)]^-$	KOCPIB	270.9(10), 271.1(12), 272.5(14), 274.5(9)	145
$[(C_6Cl_5)_2(C_6F_5)_2PtAg(tht)]^-$	KOCPOH	267.0(12), 272.9(12)	145
$[CF_3CCCF_3Ag]_4$	LAJJEL	288.9, 292.6, 292.7, 293.1, 298.6	161
$[Pt_2Ag(C_6F_5)_4(acac)_2]^-$	SUJJEM	279.5(5), 283.7(5), 284.2(5)	152
$[Pt_2Ag(\mu\text{-tht})_2(C_6F_5)_6]^-$	WEDTEE	266.3, 269.4, 278.2, 278.3, 289.6, 290.8	153
$[\{P(OPh)_3\}_2(C_6F_5)_2RhAg(PPh_3)]$	YOZWOZ	281.5(5), 286.2(5)	154
$[Pt_2Ag_4(C_6F_5)_4(\mu_3\text{-}\eta^2\text{-CCPh})_4(PPh_3)_2]$	ZEKMIL	279.1(12), 284.3(13)	155
$[\{Pt(C_6F_5)_2\}_2(\mu\text{-}C_6F_5)_2\{\mu\text{-Ag(tht)}\}]^-$	–	264.3(5), 271.6(6)	146
$[PtAg(C_6F_5)_2(acac)(CH_2Cl_2)]$	ZUYPAK	265.5(2)	156
$[(C_6F_5)_2Pt(\mu\text{-OH})\mu\text{-}\{(Ph_2P)_2CH_2\}\{Ag(PPh_3)\}Pt(C_6F_5)_2]$	–	275.4(8)–298.2(6)	157
$FN_2O_4\cdot AgCF_3SO_3$	–	271.4(3)	102

[a] Most C–F···Ag^+ angles are in the range 100–120°.

(Figure 31).[146] Variations of the complex depicted in Figure 31 were synthesized in which some of the C_6F_5 groups are substituted by C_6Cl_5 units. In the X-ray crystal structures short CCl···Ag contacts [282.7(6), 282.7(7) pm] occur, which (accounting for the larger size of chlorine) appear to be stronger than those of fluorine.[158] Other examples of short CX···metal (X = Cl, Br, I) interactions are known.[17,144,159,160]

Despite the large number of complexes with CF···Ag interactions (which are from a chemical point of view all rather similar), there is an obvious dilemma with regard to the significance of CF···metal interactions, since it is hard to see how the silver atom caught between the two platinum atoms could escape close CF···metal contacts. It is possible that the CF···metal contacts observed are vital for the existence of these compounds, but it is on the other hand not unlikely that the geometry adopted in such clusters is simply the result of a minimization of steric repulsion between the pentafluorophenyl groups. In this respect Uson and Forniés stated that the clusters with the pentafluorophenyl thiolates in general are chemically more stable than the related benzenethiolate complexes.

The excellent preorganization of the macrobicyclic donor array in the fluoro cryptand FN_2O_4 even allows the stable complexation of Ag^+ by CF donor units in solution. This was evidenced in the complex $FN_2O_4\cdot Ag^+$ by coupling between the $^{107,109}Ag$ and ^{19}F nuclei ($J = 19$ Hz).[102] Furthermore NMR competition experiments provided evidence for FN_2O_4 forming more stable silver complexes than the closely related ligand HN_2O_4, which carries a hydrogen atom in the place of the fluorine atom. Consequently it was concluded that CF···Ag interactions can significantly stabilize such complexes. In the crystal structure close CF···Ag contacts [271.4(3) pm] were also observed. Another example of weak CF···Ag contacts (292.7, 293.1, 298.6 pm, LAJJEL) was reported by Girolami et al. in the crystal of $[CF_3C(F){=}C(CF_3)Ag]_4$.[161]

3. Other Second Row Transition Elements

Other than a Ru complex reported by Cruz-Garritz et al.[162] (FAZHIX) which displays a short CF···Ru distance, only a few crystal structures with fairly long CF···metal contacts were reported in the literature. In the complex $Ru(SC_6F_4F)(SC_6F_5)_2(PMe_2Ph)_2$ with Ru(III) (Figure 33, left) the octahedral coordination sphere is completed by a fairly short CF···Ru interaction of 248.9(6) pm. Somewhat surprisingly the related Ru(II) complex $Ru(SC_6F_5)_2(PPh_3)_2$ (Figure 33, right) does not show metal–fluorine contacts, but agostic CH···Ru interactions instead.

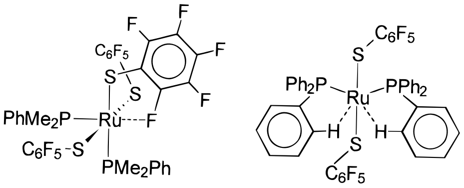

Figure 33. FAZHIX (left).

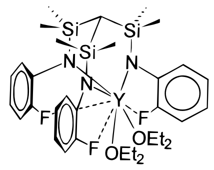

Figure 34. ZAXFAF.

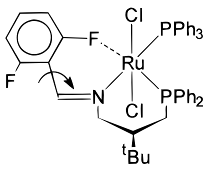

Figure 35.

Gade et al. presented a crystal structure of a tripodal yttrium complex (Figure 34) with three short CF···Y contacts [243.8(7), 248.2(6), 251.7(7) pm, ZAXDUX] and also evidenced a small coupling between $^{19}F-^{83}Y$ ($J = 5.3$ Hz) by ^{19}F NMR spectroscopy, indicative of CF···Y interactions in solution.[141]

Perera and Shaw synthesized a ruthenium complex, which on the basis of NMR data, was assigned the structure displayed in Figure 35.[163] The observation of a $J(^{31}P-^{19}F) = 68$ Hz coupling constant was considered as evidence in favor of a cis-orientation of fluorine and PPh_3 at the Ru octahedron.

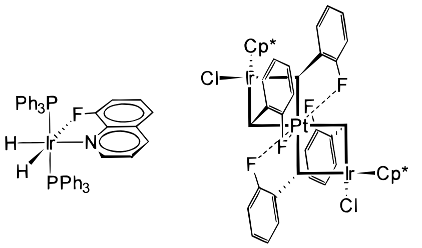

Figure 36. FIVVOV (left) and HEWYEN (right).

Other complexes with long CF···M contacts are $[Rh_2Cl_2(\mu_2\text{-}CH_2)(\mu_2\text{-}CF_3C_2CF_3)\{\mu_2\text{-}(Ph_2P)_2CH_2\}_2]$ [CF···Rh 284.3(6), 287.8(6) pm, BISVOO10],[164] $[\{Pd(\mu_2\text{-}SC_6F_5)(\mu_2\text{-}(Ph_2P)_2CH_2)Pd\}(\mu_2\text{-}SC_6F_5)]_4(Et_2O)_2$ [CF···Pd 294.5(8) pm, LAHMUC],[165] $[Pd_2(\mu_2\text{-}P^tBu_2)(CO)_2(PH^tBu_2)_2]CF_3SO_3$- [CF···Pd 274.4, 278.0 pm, LANNAP],[166] $Cd\{2,4,6\text{-}(CF_3)_3C_6H_2\}_2$ [CF···Cd 279.7(6), 289.2(6), 293.1(8) pm, VOTGIU],[128] and $Cd(C_6F_5)_2$ [CF···Cd 297.3(8) pm, intermolecular contact, WACCAE].[167] Espinet et al. characterized two $Pd\{2,4,6\text{-}(CF_3)_3C_6H_2\}_2$ (TASWUF, TASXAM) complexes in which the authors considered CF···Pd distances equal to or larger than 289.7 pm as nonbonded contacts.[168]

C. Third Row Transition Elements La–Hg

Examples of interactions between CF units and these metals are rare and $Ir(H)_2(PPh_3)_2$(8-fluoroquinoline) by Holt, Crabtree, et al. (Figure 36, left) is basically the only structurally characterized complex. In this crystal structure an exceptionally short CF···Ir distance of 251.4(8) pm (FIVVOV) was observed.[169] The octahedral coordination geometry involving CF coordination seems to persist in less polar solvents as is indicated by NMR coupling via iridium with a $^2J(^1H-^{19}F) = 10.3$ Hz. Strong evidence for an attractive CF···Ir interaction comes from the IR spectrum as the ν(C–F) is shifted to 1231.6 cm^{-1}, which is a long wave shift of 14 cm^{-1} relative to free 8-fluoroquinoline.

Examples of the interaction of fluorohydrocarbons with $W(CO)_5$ in the gas phase have been reported, even though it was not known with certainty whether CF···W or CH···W contacts are preferred.[170] Very recently an experimental investigation by Dobson et al.[171] and a theoretical study by Hall et al.[172] provided clear evidence in favor of CF···W interactions.

The photolytic generation of $M(CO)_5$ species (M = Cr, Mo, W) in fluorocarbons leads to aggregates of the type $(CO)_5M\cdots F-R_F$ which were probed by infrared spectroscopy at low temperatures,[173] UV/VIS spectroscopy,[174] or photoacoustic calorimetry.[175] A more detailed discussion of the interaction of unsaturated organometallic fragments with fluorocarbons was given in a recent review by Hall and Perutz on transition metal alkane complexes.[176]

In the few other complexes which display CF···metal distances below the 300 pm threshold, evidence in favor of significant CF···metal interactions is not very convincing: Two platinum–iridium–pentafluorobenzenethiolate complexes by Castellano et al. display four short CF···Pt contacts, respectively, in the range of 298.3–304.4 pm (HEWYIR) and 299.3–307.5 pm (HEWYEN) (Figure 36, right, only fluorine atoms coordinated to Pt are drawn, all other fluorine atoms are omitted).[177] Two platinum–mercury–pentafluorophenyl complexes reported by Uson et al. are structurally closely related to the platinum–silver complexes from the same authors and display short CF···Hg contacts [281(3), 287(3), 295(3), 299(3), 300(3) pm, YANNER; 298.5(8) and others longer than 300 pm, YAYNAN].[178]

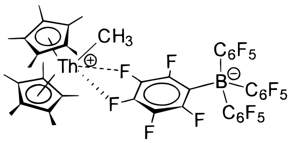

Figure 37. KIRYOZ.

V. Complexes of the Lanthanides and Actinides

Despite the hardness of these metal ions only a few examples of reasonably short metal–fluorine interactions (i.e., shorter than 300 pm) were found and this appears to be due to the relative dearth of complexes with these metals.

San Filippo and co-workers may have been the first who hinted at a special kind of CF···metal interaction.[179] Upon monitoring the ^1H NMR spectra of fluorinated hydrocarbons like *n*-octylfluoride in the presence of the shift reagents $Eu(fod)_3$ and $Yb(fod)_3$, they noticed that the metal-induced shifts of the ^1H NMR resonances decrease as the average distance from the fluorine nucleus under observation increases. In order to account for this observation the formation of a CF coordinated lanthanide–fluoroalkane complex was postulated.

More convincing evidence was presented by Marks et al. who realized that the olefin polymerization activity of cationic $(Cp^*)_2ThCH_3^+$ complexes depends crucially on the nature of the counter ion.[135,180] Consequently with $B(C_6F_5)_4^-$ a 3300-fold increase in the rate of ethylene polymerization was observed in comparison to the activity in the presence of $B(C_6H_5)_4^-$. This evidence was rationalized with data from X-ray crystal structure analysis which show the thorium cation coordinated by two CF units from a single C_6F_5 ring (Figure 37). The CF···Th distances are 267.6(5) and 275.6(4) pm (KIRYOZ), which are significantly longer than the sum of the respective ionic radii (ca. 228 pm).

$Pr(O(CH_3)_2CF_3)_3$ was structurally characterized by Bradley et al. and shown to possess CF···Pr interactions [275(1), 276(1), 277(1), 300(1) pm, PAJJIT].[181]

VI. Complexes of the Main Group Metals

The large number of crystal structures of main group metal complexes (especially of Ga, In, Sn, and Pb) with the ligand $2,4,6\text{-}(CF_3)_3C_6H_2$- ($=R_F$) is the main reason for the correspondingly large number of CF···metal contacts observed. These CF···metal interactions may not be strong but nonetheless appear to exert a subtle influence on the stability of some compounds. A detailed discussion of the structurally closely related complexes is therefore not deemed necessary but a closer look should be taken at the R_F ligand.

The 2,4,6-tris(trifluoromethyl)phenyl ligand has found widespread use in main group chemistry and

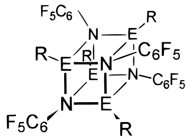

Figure 38. E = Ga, In.

this field was reviewed by Edelmann.[182] Its unique properties with respect to the stabilization of unusual bonding situations are believed to result from a combination of factors such as high steric demand, electron-withdrawing effect, and additional stabilization from the neighboring CF_3 groups and their lone pairs, which can favorably interact with metal cations. Again it could be argued that short CF···metal contacts are inevitable in complexes with this ligand. However, even though in the alkali metal complexes several unusual structures provide evidence that some of the unique properties of this ligand result from attractive CF···metal interactions, it appears likely that the interactions of the CF_3 groups with transition metals and late main group metals are more subtle.

The large number of crystal structures of fluorinated ligands with the elements Ga, In, Tl, Ge, Sn, Pb, and Bi requires a reasonable distance threshold for the selection of the crystal structures with CF···metal contacts. For this purpose the main group metal–oxygen bond lengths observed in complexes with macrocyclic polyethers have been analyzed, because it is anticipated that the oxygen–metal distances can serve as reasonable models for CF coordination. In the crown ether complexes of Tl salts most metal–oxygen distances are in the range between 260 and 310 pm. For Ga, In, Ge, Sn, Sb, and Bi complexes with macrocyclic polyethers most metal–oxygen distances are smaller than 300 pm. Consequently we have set the threshold up to which CF···metal interactions are considered in this review: for CF···Tl $<$ 320 pm, for Pb, Bi, Ge, Sn $<$ 310 pm and for Ga, In, Sb $<$300 pm.

A. Gallium and Indium

A significant number of crystal structures of gallium and indium complexes featuring short CF···Ga, In contacts is known. However, all compounds represent variations of two basic chemical motifs, of which examples are displayed in Figure 38 and Figure 39.

Three crystal structures belonging to the first group of compounds were described by Roesky et al. and the characteristic feature of these complexes is a tetrameric E_4N_4 cube (E = Ga, In) with short CF···Ga or CF···In contacts [CF···Ga 290.1, 291.2, 292.0, 295.5, 298.2 pm, PEMMUP; CF···In 284.3, 285.4, 290.3, 291.3, 296.9 pm, PEMNAW; CF···Ga 281.1, 284.0, 287.8, 292.7 pm, YEXYEF].[183,184] Four crystal structures of the second group were reported by Cowley et al. in which the R_F ligand [$R_F = 2,4,6\text{-}C_6H_2(CF_3)_3$] is bonded to Ga(III) or In(III): [ClGa(R_F)$_2$]$_2$ (270.0, 273.6 pm, POMTUG), [Cl(OH)GaR$_F$]$_2$ [271.8, 272.0, 274.5, 278.1 pm, POMVAO], Ga(R_F)$_3$ [267.8, 268.3, 271.1, 277.5, 278.3, 282.1 pm, POMVES], (R_F)$_3$In [six contacts, 271.7(7)–279.8(5) pm, YANCAR], and (R_F)$_2$In–In(R_F)$_2$ [eight contacts, 280.1(10)–295.7(13)].[185,186]

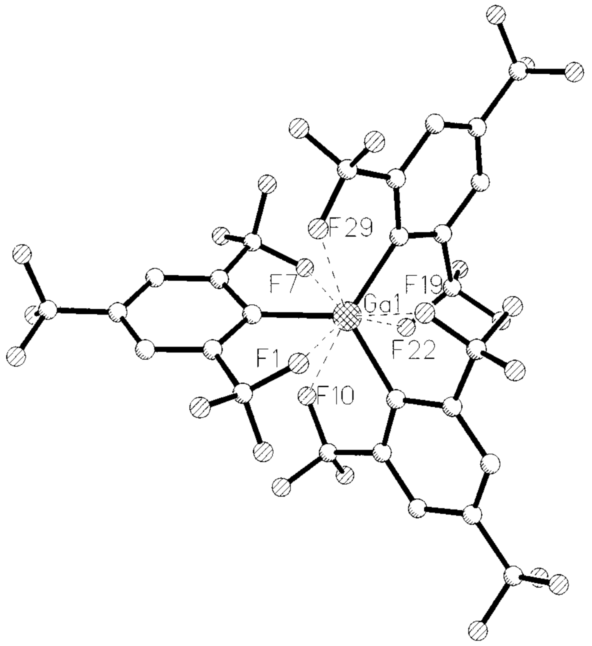

Figure 39. Crystal structure of POMVES (hydrogen atoms omitted).

B. Thallium

Thallium is an interesting element with respect to CF···metal interactions, because it consists of the two isotopes ^{203,205}Tl which are fairly sensitive NMR nuclei and because its coordination chemistry is somewhat related to that of potassium.

An example with CF···Tl interactions presented here is [$(C_6F_5)_4$Pt–Tl–Pt$(C_6F_5)_4$]$^{2-}$ from the Uson group, which was the first Tl(II) compound ever.[187] In this paramagnetic complex eight CF···Tl contacts from the eight adjacent pentafluorophenyl rings were found [CF···Tl, eight contacts 283.9(10)–306.5(12) pm, YOKFOT]. As already discussed for related silver complexes it is very difficult to decide whether such close CF···Tl contacts are stabilizing or simply the result of a sterically favorable arrangement of the C_6F_5 rings (Figure 40).

The mixed alkoxide $Na_2Zr(OCH(CF_3)_2)_6$ described by Caulton et al. displays short CF···Na$^+$ contacts in the solid state and it was hoped that the replacement of sodium by thallium would result in a clear cut case of stabilizing CF···Tl contacts.[37,188] As expected in the crystal structure of $Tl_2Zr(OCH(CF_3)_2)_6$ numerous CF···Tl contacts were observed [306.8(8), 309.7(8), 313.6(12), 321.4(11), 323.8(11), 328.7(11), 328.9(11) pm, PANHUH10]. Furthermore, the presence of CF···Tl interactions in solution was indicated by ^{19}F–^{203,205}Tl coupling. The complex multiplet displayed in the ^{205}Tl NMR spectrum was calculated to result from coupling with 36 equivalent spin-$^1/_2$ nuclei with a coupling constant of 388 Hz. The ^{205}Tl NMR results thus provide evidence for the metal ion migrating rapidly over all eight ZrO_3 triangular faces. Davidson, Lindsell et al. reported two structures which display short CF···Tl contacts in solution as well as in the solid state, which were already described in the cesium section.[78]

Other examples of crystal structures with short CF···Tl interactions are hydrogen (tris(3,5-bis(trifluo-

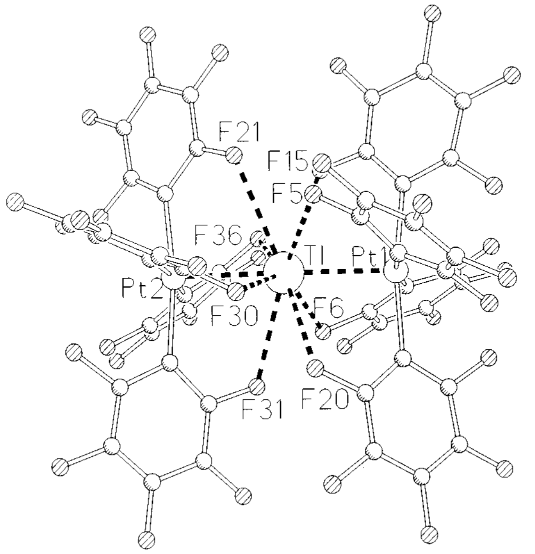

Figure 40. Crystal structure of YOKFOT.

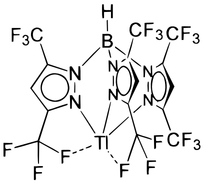

Figure 41. ZAGSAB.

romethyl)pyrazol-1-yl)borate)−thallium (Figure 41) [311.6, 326.6 pm, ZAGSAB],[189] $Tl[\{3,5\text{-}(CF_3)_2C_6H_3\}_4B]$ [305(6), 318(6) pm],[190] thallium hexafluoroacetylacetonate [307.3, 321.5 pm, HFACTL],[191] $[Tl(SR_F)]_x$ [312.5, 313.1, 317.5, 325.2 pm, SIZBEI],[192] $[(p\text{-}HC_6F_4)_2\text{-}TlCl(OPPh_3)]_2$ [313.6, 316.7 pm, CFPOTL],[193] polymorph from $WCl_2(PMe_2Ph)_4$ and $[TlOCH_2CF_3]_4$ [312.0, 318.7, 322.1, 323.7, 327.2 pm, LAYKEB; 312.3, 320.4, 320.9, 326.2 pm, LAYKEB01],[194] *cis*-$[Tl(\mu_2\text{-}OOCCH_3)\text{-}Pt(PPh_3)(C_6F_5)_2]$ [298.2(9) pm],[195] and $(NBu_4)_2[\{Pt(C_6F_5)_3\}_2\{(\mu_2\text{-}O,\mu_2\text{-}O'CCH_3)Tl\}_2]$ [304.0(5)−308.1(5) pm].[195]

C. Germanium, Tin, Lead, and Bismuth

Numerous complexes of Sn, Pb, and Bi with short CF···metal distances are known, but as stated before, this probably only reflects the large number of complexes with the 2,4,6-$(CF_3)_3C_6H_3$ ligand. Two examples for short CF···Sn distances are the monomeric yellow stannylene (Figure 42) $(R_F)_2Sn$ [266.3(4), 268.1(4), 280.7(4), 283.3(4) pm, KILHAO],[196] which also exists as a Sn−Sn bonded red dimer [268.8(6), 271.1(6), 280.3(6), 282.6(6) pm, KILHAO01].[197] In the complex by Grützmacher the ^{119}Sn and ^{19}F nuclear spins are coupled and it is interesting that this coupling constant increases upon lowering the probe temperature. The X-ray crystal structure of $(R_F)_2Ge$ which was described recently by Holl et al. is also characterized by short CF···Ge interactions [255.4(1), 256.6(2), 278.2(2), 279.0(1) pm].[198]

Other crystal structures with close CF···M (Sn, Pb, Bi) contacts are as follows.

CF···Sn: KIJKIX [10 contacts 289.0(15)−325.3(20) pm],[199] DURWES [301.5, 316.4 pm],[200] JOSHII [272.3, 302.4, 304.4, 322.7, 328.8 pm],[201] LIMYOV [271.3, 281.4, 294.1, 295.1 pm],[202] PILVUB [272.9, 273.1, 274.0, 274.1, 321.8 pm],[203] VIZPEZ [276.8, 279.1, 284.2, 289.2, 294.7, 296.4 pm],[204] VOGNUA [268.6, 273.5, 285.2, 285.9, 296.9, 304.1, 321.4 pm],[205] WEDTOO01 [20 contacts 265.5−328.7 pm],[206] Shreeve [297.2, 307.4 pm].[207]

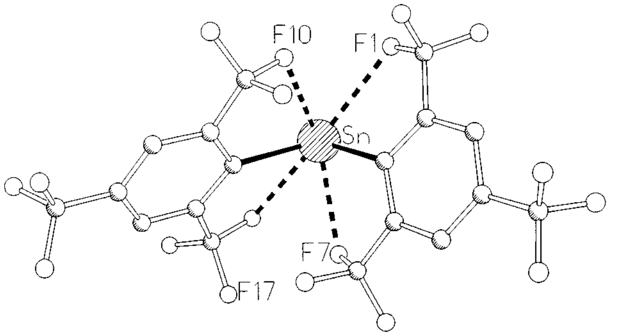

Figure 42. Crystal structure of KILHAO (hydrogen atoms omitted).

CF···Pb: VUPKAS [eight contacts 276.1(2)−299.6(2) pm],[208] ZIWKAR [six contacts 286.4(8)−301.8(9)], and ZIWJUK [five contacts 281.7(5)−303.2(6)],[209] KILMEX [278.4, 279.3, 284.0, 296.7, 325.1 pm],[210] PIKSEH [CF···Pb 314.2, 313.9, 308.9, 305.7 pm].[211]

CF···Bi: Bi-SC_6F_5 complexes [307.1(7) pm, WAYYEA],[212] $ClBi(R_F)_2$ [288.5, 289.0, 303.9, 306.5, 316.7, KIMJEV], $Bi(R_F)_3$ [286.7, 292.2, 293.9, 324.1, 329.8, KIMJIZ],[213] YUKSAY [294.0 pm].[69]

VII. On the Possibility of CF···HN and CF···HO Hydrogen Bonds

Hydrogen bonding is of fundamental importance in chemistry and biology alike[214] and because of this the question of possible CF···HN or CF···HO interactions was raised by Glusker in 1983.[10] It was suggested that there was a chance for such interactions to occur under special circumstances and consequently H bonding involving fluorine as a proton acceptor has been postulated in inhibitor complexes of elastase.[215] More detailed investigations on the strength of the internal CF···HO hydrogen bond in 3-fluoropropanol,[216] 2-fluoroacetaldehyde,[217] fluoropropionic acid,[218] and tetrafluorohydroquinone[219] were indicative of very weak interactions.[220] Ab-initio calculations by Dixon and Smart[221] on 2-fluoroethanol revealed a small stabilization of the gauche isomer due to internal hydrogen bonding measured at 1.9 kcal/mol.[217] However, based on MP2/6−31++G** calculations, FT-IR and NMR spectroscopic results Bakke et al. pointed out that this gauche preference is not due to the very weak hydrogen bonding, since repulsive forces between lone pairs are much stronger.[222] Hydrogen bonding to covalent transition metal fluorides is also known and the work in this field was summarized by Richmond.[223]

Hydrogen bonding involving fluorocarbons has received more attention[224] in two theoretical and one experimental study by Glusker et al.,[225] Dunitz and Taylor[226] and Plenio and Diodone.[227] High quality ab-initio calculations[228] on complexes of CH_nF_m ($n + m = 4$) with NH_4^+ indicated weakly stabilized ag-

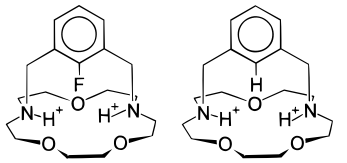

Figure 43. $FN_2O_3{\cdot}2H^+$ (left) and $HN_2O_3.2H^+$ (right).

gregates. The energy for the dissociation of the complex $H_3CF\cdots H_4N^+$, in which the $CF\cdots HN$ unit is almost linear, was calculated as $\Delta H^\circ_{298} = 13.5$ kcal/mol (in the gas phase!). For $H_2CF_2\cdots H_4N^+$ and $HCF_3\cdots H_4N^+$, however, the dissociation energy per $CF\cdots H$ interaction drops significantly due to increasing deviations from the linear geometry.[225]

Dunitz and Taylor performed an extensive analysis of crystal structures in the CSD and out of 5947 CF bonds only 37 (i.e., 0.6%) are involved in possible $CF\cdots HX$ (X = O, N) interactions. A critical analysis of the few remaining candidates showed that only two examples can be regarded as unequivocal hydrogen bonds. This scarcity of data is indicative of covalently bound fluorine being a poor hydrogen-bond acceptor. This view is backed by quantum mechanical (IMPT) calculations. Somewhat in contrast, the conventional view of hydrogen bonding—according to Bernstein—is that of an essentially electrostatic type of interaction,[229] which would allow CF units to form stable hydrogen bonds. However, Dunitz and Taylor put forward that the observed extremely weak tendency of covalently bonded fluorine to form hydrogen bonds can be attributed to a combination of two factors: its low proton affinity (low basicity, low-lying lone pair orbitals, tightness of its electron shell) and its inability to modify this by intermolecular electron delocalization or intermolecular cooperative effects.[226]

In the third study by Plenio and Diodone an experimental approach was chosen by investigating the protonation of fluoro macrocycles and by comparing the properties of these materials with those of reference compounds, which differ only with respect to a single fluorine atom (Figure 43).[227]

For this investigation the relative basicities of fluorine-containing and fluorine-free cryptands, their X-ray crystal structures, infrared spectra, and ^1H, ^{13}C, and ^{19}F NMR spectra were analyzed. However, the results from this study were inconclusive in so far as clear experimental proof in favor of $CF\cdots HN$ interactions could not be obtained. It was thus finally concluded: Should an interaction between $CF\cdots HN^+$ exist, it is certainly going to be of a very weak nature.

VIII. Recurring Structural Motifs in the Coordination Chemistry of the CF Unit and Concluding Remarks

After summarizing the literature on CF···metal contacts it was deemed necessary to analyze this information and to extract basic chemical motifs to gain a better understanding of the coordination chemistry of the CF unit in fluorocarbons. Such a collection of the most relevant substructures with typical ligands in CF···metal coordination is given in Figure 44.

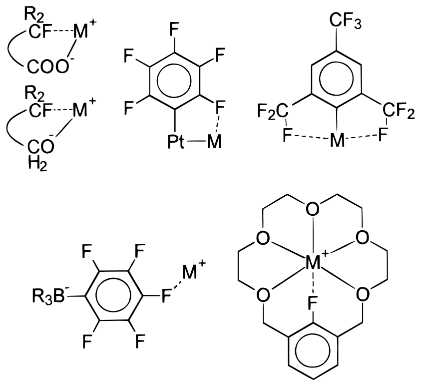

Figure 44.

Based on this a general recipe with the essential ingredients for CF···metal interactions can be derived, which is presented as a short summary.

The ligands contain many fluorine atoms, but only few other (potential) donor atoms. The competition between oxygen and fluorine donors for the coordination of metal ions will generally favor oxygen. In the absence of other donor atoms, the metal ion has to complete its coordination sphere with CF donors. A slight disadvantage of perfluorination is that each fluorine is surrounded by electron-withdrawing substituents, which will reduce the partial negative charge at individual fluorine atoms and consequently the strength of the dipole–cation interaction.

The fluorinated ligand has a negative charge. A negatively charged ligand will improve the electrostatic interaction with a metal cation. In less polar solvents the formation of close ion pairs between ligand and metal cation will enhance CF···metal interactions.

C*helation can be very useful.* To promote CF···metal interactions in solution, it is advantageous for the CF unit to be part of a chelating ligand, which is already bonded to the metal center via a strong bond.

The CF unit is part of an efficiently preorganized, macrocyclic or macrobicyclic donor array. In metal complexes of fluoro macrocycles the oxygen donors may help to hold the metal ion in a favorable orientation with respect to the CF donor units. The better the preorganization of the donor atoms, the stronger the effect of CF···metal coordination. In such ligands CF···metal interactions persist in polar solvents.

The coordination of group I and II metal ions is preferred. The large number and the variety of structural types found in complexes of the alkali and alkaline earth metal ions with fluorinated ligands shows that the coordination of hard metal ions by CF units is strongly favored with respect to other softer metal ions.

It can thus be concluded that while the strength of the CF···alkali metal interaction in fluorocarbons is certainly weaker than that of an ether oxygen,[230] it is, nevertheless, far from negligible and given a suitably preorganized array of donor atoms it can be quite significant. In this respect it must be noted that the preorganization of donor atoms is very important in the coordination chemistry of alkali metal ions in general, not only with CF donor units. Consequently, prior to Pedersen's and Lehn's discovery of the highly preorganized crown ethers and cryptands, stable complexes with these metal ions used to be rare.[231]

IX. Acknowledgments

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Note Added in Proof

Some recently published articles on this topic are included for reference. CF···Co: Chen, Q.; Lin, C. Y.; Chen, H.; Freiser, B. S. *Organometallics* **1997**, *16*, 4020. CF···Zr: Karl, J.; Erker, G. *Chem. Ber.* **1997**, *130*, 1261. CF···Zr: Pinado, G. J.; Thornton-Pett, M.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1997**, 3115.

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