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Concepts in the NMR structural analysis of perfluoroalkyl groups: characterization of the bis(n-perfluoroalkyl)zinc compounds $Zn(n\text{-}C_mF_{2m+1})_2{\cdot}2THF$ ($m = 4, 6, 7, 8$) and $Zn(n\text{-}C_6F_{13})_2{\cdot}2CH_3CN$

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Dedicated to Professor Marianne Baudler on the occasion of her 80th birthday.

Abstract

Two-dimensional NMR spectroscopy was used in the structural characterization of the bis(n-perfluoroalkyl)zinc compounds $Zn(R_f)_2{\cdot}2D$ with $R_f = n\text{-}C_4F_9$, $n\text{-}C_6F_{13}$, $n\text{-}C_7F_{15}$, $n\text{-}C_8F_{17}$; D = tetrahydrofuran and $R_f = n\text{-}C_6F_{13}$; D = acetonitrile. Since $^4J(^{19}F, ^{19}F)$ is the strongest coupling occurring in the ^{19}F spin system of n-perfluoroalkyl ligands, CF_x groups in 1,3-position could be identified by ^{19}F, ^{19}F correlation spectroscopy (COSY). In this way the complete information on neighborhood relations in the $n\text{-}C_mF_{2m+1}$ chain is cut into two series of ^4J connected CF_x groups. Important information how these two series must be joined together was obtained from the assignment of the CF_3 group signal (relative intensity), from weak ^{19}F, ^{19}F couplings (resulting from interactions via three, five, or even six bonds), and from ^1J-^{13}C, ^{19}F correlations, which characterize the α-CF_2 group by the typical downfield shift of the metal substituted carbon atom. When this information was not sufficient, ^{13}C,^{19}F correlations via one and two bonds were carried out to identify directly neighboring CF_x groups. It was demonstrated that this type of two-dimensional correlation spectroscopy provides an independent and unambiguous possibility to characterize the constitution of perfluoroalkyl groups. From the obtained chemical shift values the following characteristic trends were deduced. The CF_3 group exhibits the most downfield and the neighboring CF_2 group the most highfield ^{19}F chemical shift values. The subsequent CF_2 groups up to the CF_2 group in β-position to the Zn atom show increasing $\delta(^{19}F)$ values. The resulting sequence of signals is only interrupted by the resonance of the α-CF_2 group appearing at a not well-defined position. In the ^{19}F decoupled ^{13}C spectrum the peak of the α-CF_2 group constitutes the most downfield shift value. The ^{13}C resonances of the remaining CF_2 groups, although falling into a very narrow range, are shifted to higher field with increasing distance from the Zn atom. The signal of the CF_3 group, appearing between those of the α- and β-CF_2 groups, is well characterized by its chemical shift (very close to 118.8 ppm) and by its different phase in the $^{13}C\{^{19}F\}$ DEPT 135 spectrum. Thus, a well-defined relation between ^{13}C chemical shifts and structure was established. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: NMR spectroscopy; ^{19}F, ^{19}F and ^{13}C,^{19}F NMR correlations; Perfluoroalkyl zinc compounds; Structural determination

1. Introduction

The NMR spectroscopic structure elucidation of perfluoroalkyl groups is usually based on the analysis of the ^{19}F, ^{19}F coupling network. ^{19}F chemical shifts also provide structural information. Thus, ^{19}F chemical shifts have been correlated with different structural parameters [1–3] and structural units [4–8]. The latter correlation was used to evaluate increment systems in the determination of ^{19}F chemical shift values.

Still, the most important structural information results from $^4J(^{19}F, ^{19}F)$, which is the largest coupling occurring in the ^{19}F spin systems of perfluoroalkyl groups [9] (except vicinal ($^2J(^{19}F, ^{19}F)$) couplings, which are usually not observed). With increasing length of the perfluoroalkyl chain small ^{19}F, ^{19}F couplings lead to complex and badly resolved splitting patterns, which prohibit a classical spin analysis. This problem has been overcome by two-dimensional ^{19}F, ^{19}F correlation spectroscopy [10] because even unresolved coupling leads to cross peaks if the relaxation time T_2 is not too small in comparison to $1/(2J)$.

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Since $^4J(^{19}F, ^{19}F)$ is the strongest coupling, the standard pulse sequence of homonuclear correlation spectroscopy (COSY [11,12]) generates cross peaks between CF_x groups in 1,3-position. Thus, if the CF_x groups are numbered according to their position in an unbranched chain, the signals of CF_x with odd numbers make up one series of *J*-connected peaks, those with even numbers the second series. In order to obtain the constitution of the complete perfluoroalkyl chain the two independent sequences of connectivities must be joined together in the correct way. The solution of this problem may be found in different ways. The lacking information on neighborhood relations between CF_x groups from different series (odd or even) may be taken from less intense cross peaks resulting from weak couplings. Furthermore, specific ^{19}F chemical shifts may be used to gain additional information; also ^{13}C chemical shifts may help, if the corresponding CF_x group is characterized by ^{13}C, ^{19}F correlation. [13,14].

Finally, the combination of ^{13}C, ^{19}F correlations via one and two bonds provides an independent method to characterize the constitution of perfluoroalkyl groups [14]. Since the condition $^1J(^{13}C,^{19}F) \gg {}^2J(^{13}C,^{19}F) \gg {}^3J(^{13}C,^{19}F)$ is met for this class of compounds, ^{13}C and ^{19}F nuclei connected by ^1J and ^2J coupling may clearly be identified. This directly leads to the unambiguous determination of neighboring CF_x groups.

In the present contribution ^{19}F, ^{19}F and ^{13}C, ^{19}F correlation spectroscopy has been used in the complete assignment of the ^{19}F and ^{13}C spectra of the bis(*n*-perfluoroalkyl)zinc compounds $Zn(n\text{-}C_mF_{2m+1})_2\cdot 2THF$ $(m = 4, 6, 7, 8)$ and $Zn(n\text{-}C_6F_{13})_2\cdot 2CH_3CN$. The synthesis of these compounds has already been published elsewhere [15].

2. Experimental details

The bis(*n*-perfluoroalkyl)zinc compounds $Zn(n\text{-}C_mF_{2m+1})_2\cdot 2THF$ with $m = 4, 6, 7, 8$ as well as $Zn(C_6F_{13})_2\cdot 2CH_3CN$ were prepared as described previously [15]. The NMR spectra were recorded on saturated solutions (22°C) in d_8-tetrahydrofuran (and d_3-acetonitrile in the case of $Zn(C_6F_{13})_2\cdot 2CH_3CN$) at a temperature of 25°C. In the case of the perfluorobutyl and perfluorohexyl compounds a Bruker AC 200 (^{19}F COSY) and a Bruker AMX 300 (^{13}C, ^{19}F correlation) were used. The low band coil of the 5 mm quadruple probe head of the AC 200 F was tuned to the ^{19}F frequency of 188.13 MHz (length of the 90°pulses: 6.3 μs). The ^{19}F COSY spectra were acquired between −80 and −135 ppm (corresponding to a spectral window of 10.90 kHz) using 2 K data points in t_2 and 512 time increments in t_1 with 32 scans for each FID. After zero filling and application of an unshifted squared sine function in t_2 and t_1 the $1\,K \times 1\,K$ data matrix was Fourier transformed into a $1\,K \times 1\,K$ data matrix in the frequency domain (absolute value mode).

The HMQC method [16,17] was adopted to record single and two bond ^{13}C, ^{19}F correlated spectra. $^2J(^{13}C,^{19}F)$ coupling constants vary between 30 and 60 Hz and the delay 1/(2*J*) in two bond correlation was optimized to an intermediate value. Cross peaks resulting from ^1J couplings (250–300 Hz) are not generally suppressed by this delay. Nevertheless, since no decoupling was applied during data acquisition ^1J cross peaks can easily be distinguished from ^2J cross peaks by their large splitting into doublets along the ^{19}F axis (no ^{13}C, ^{19}F coupling occurs along the ^{13}C axis because it does not develop during t_1). Although the HMBC method [18] is frequently used in ^2J correlation in order to eliminate cross peaks resulting from ^1J coupling, we did not achieve any advantage by this pulse sequence. We also did not use a BIRD filter [19] because the T_1 values of the CF_3 and CF_2 groups may differ by the factor of four (see Table 1).

The HMQC spectra were acquired using a 5 mm inverse broad band probe head with the high band coil ($^1H/^{19}F$) tuned to the ^{19}F frequency of 282.35 MHz and the broad band coil (^{31}P-^{109}Ag) tuned to the ^{13}C frequency at 75.47 MHz (length of the 90° pulses: 9.8 μs (^{19}F) and 14.0 μs (^{13}C)). Two separate experiments were carried out for each compound. The first one correlated the ^{13}C resonances (100–135 ppm) with the ^{19}F region of the CF_2 group resonances (−130 to −115 ppm) and the second one correlated the same ^{13}C region with the ^{19}F signal of the CF_3 group (using a ^{19}F spectral width of 1 kHz). The data were collected and processed in the absolute value mode. 512 Increments were used in the t_1 dimension collecting 16 scans for each FID of 2 K data points. The experimental data matrix was zero filled to a size of $1\,K \times 1\,K$ and processed (using a shifted squared sine function (SSB = 2.5) in t_2 and in t_1) into a final data matrix of size $1\,K \times 1\,K$ $(f_1 \times f_2)$.

The homo- and heteronuclear correlated spectra of the perfluoroheptyl and perfluorooctyl compounds were recorded on a Bruker DRX 500 spectrometer using a 5 mm inverse broad band probe head equipped with a field gradient coil. The high band coil ($^1H/^{19}F$) of the probe head was tuned to the ^{19}F frequency of 470.59 MHz and the broad band coil (^{31}P-^{109}Ag) was tuned to the ^{13}C frequency at 125.75 MHz (lengths of the 90° pulses: 9 μs (^{19}F) and 11 μs (^{13}C)). The ^{19}F COSY spectra were acquired at a spectral width of 26 kHz using field gradients for phase selection. 2 K Data points were collected in the t_2 domain and 512 time increments in the t_1 domain (two scans for each FID). Data acquisition ($0.5\,K \times 2\,K$ data matrix) and processing were carried out in the absolute value mode (size of the final

Table 1
T_1 values of the ^{19}F spins of Zn $(C^1F_2C^2F_2C^3F_2C^4F_2C^5F_2CF_3)_2$ determined by an inversion recovery experiment using the simple equation $T_1 = t_0/\ln 2$ (^{19}F frequency = 282.35 MHz)[a]

	C^1F_2	C^2F_2	C^3F_2	C^4F_2	C^5F_2	CF_3
T_1 (s)	0.4	0.7	0.58	0.78	1.23	1.85

[a] At the time t_0 the magnetization inverted by the 180° impulse becomes zero.

matrix: 1 K × 2 K). Prior to Fourier transformation an unshifted squared sinusoidal function was applied in t_2 and in t_1 domain. The ^{13}C, ^{19}F correlation via ^1J and ^2J couplings were carried out using the HMQC method as described above. In the single bond correlation the complete range of the ^{13}C resonances (105–145 ppm corresponding to a spectral width of 5 kHz) was correlated with the ^{19}F region of the CF_2 resonances (−116 to −128 ppm corresponding to a spectral width of 4.7 kHz). Field gradients were used for phase selection and ^{13}C decoupling was applied during acquisition. The experimental data were acquired in a 0.5 K × 2 K ($t_1 \times t_2$) data matrix collecting 24 scans for each time increment. After zero filling and applying a $\pi/2$-shifted squared sinusoidal weighting function in both dimensions the data were transformed into a 1 K × 2 K final data matrix. The two bond correlation was accomplished in the same way optimizing the delay $1/(2J)$ to a value of 11 ms and using a 0.5 K × 4 K acquisition data matrix. Thirty-two scans were collected for each FID. Furthermore, no decoupling was applied during acquisition, so that cross peaks resulting from ^1J coupling could easily be identified by their large splitting into doublets along the ^{19}F axis. Processing was performed with a 1 K × 4 K final data matrix applying Gaussian multiplication in t_2 domain and an unshifted squared sinusoidal function in t_1 domain.

3. Results and discussion

3.1. *Bis(nonafluorobutyl)zinc $Zn(n\text{-}C_4F_9)_2\cdot 2THF$, strategies of spectra analysis*

The advantages and the limitations of ^{19}F, ^{19}F J-correlation can be demonstrated by the example of the COSY (90) spectrum of $Zn(n\text{-}C_4F_9)_2\cdot 2THF$ (Fig. 1). The strong and weak cross peaks observed in the spectrum are summarized below (weak cross peaks are given in parentheses).

Signal	Cross peaks with signal
A	B (C)
B	A (C, D)
C	D (A, B)
D	C (B)

With the assumption $^4J(^{19}F,^{19}F) > {}^3J(^{19}F,^{19}F) \cong {}^5J(^{19}F,^{19}F)$ the connectivities A–O–B and C–O–D (O resembles an unspecified CF_2 group or its NMR signal) may be deduced from the strong cross peaks. Furthermore, from the chemical shift and the relative intensity in the one-dimensional spectrum signal A can be attributed to the CF_3 group. Consequently, B must be assigned to the C^2F_2 group whereas C and D may be assigned in two different ways as shown in Scheme 1.

In principal, the remaining question in signal assignment may be solved with the aid of weak cross peaks resulting from ^3J or ^5J couplings. The weak cross peaks of B with C and D are in agreement with both alternatives of signal assignment. For geometric reasons they must correspond to ^3J couplings. The signal of the CF_3 group A shows only one weak cross peak, which leads to signal C. If we knew, whether this cross peak corresponds to a ^3J or to a ^5J coupling, the true assignment could be found. Indeed it has been reported that CF_3 groups in perfluorinated hydrocarbons show ^{19}F, ^{19}F couplings only via four and five but not via three bonds [14,20]. This would support the assignment given in the first line of Scheme 1. But on the other hand, it did not appear adequate to establish signal assignment on the basis of one weak cross peak only.

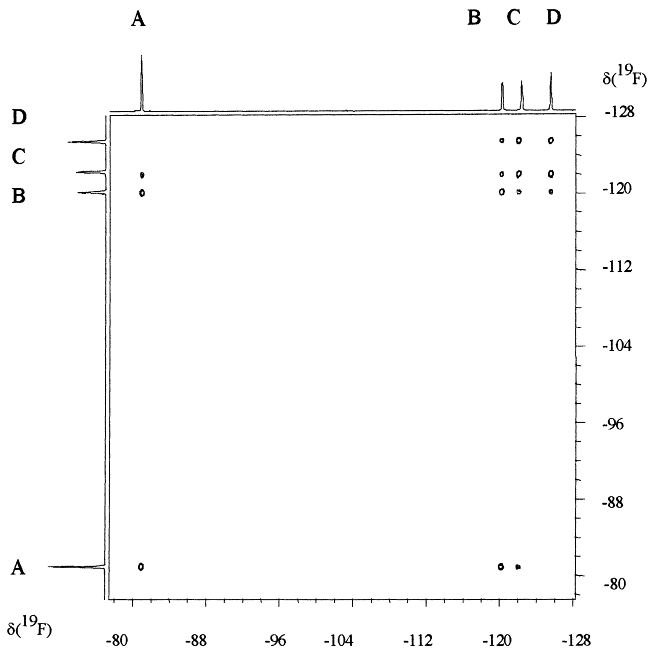
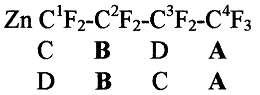


Fig. 1. 188.13 MHz ^{19}F COSY spectrum of $Zn(n\text{-}C_4F_9)_2\cdot 2THF$ in d_8-THF.

The uncertainty in signal assignment from the ^{19}F COSY spectrum of a perfluoroalkyl group is a general problem, which results from the condition that $^4J(^{19}F,^{19}F)$ is the strongest coupling occurring in the ^{19}F spin system and that fluorine, fluorine interactions over three, five and sometimes even six bonds cannot be distinguished from each other. Thus, additional information is needed, which may be obtained from ^{13}C, ^{19}F correlation spectroscopy.

Most frequently the identification of directly bonded fluorine and carbon atoms, which is carried out by ^1J-^{13}C, ^{19}F correlation may provide the missing information. In the case of zinc perfluoroalkanes, the zinc atom strongly deshields the α carbon atom leading to a characteristic downfield shift of C^1. Thus, ^1J-^{13}C, ^{19}F correlation has


Zn C^1F_2-C^2F_2-C^3F_2-C^4F_3
C **B** D **A**
D **B** C **A**

Scheme 1.

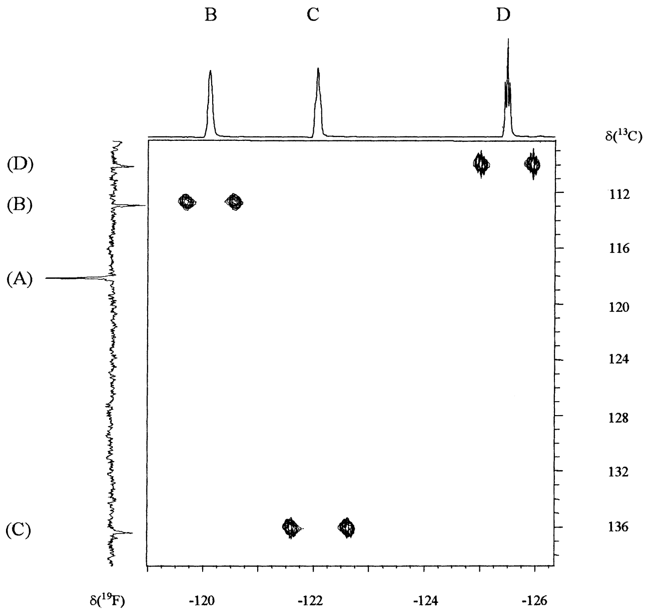


Fig. 2. ^{19}F detected (CF_2 groups only) ^1J-^{13}C, ^{19}F correlated NMR (HMQC) spectrum of Zn(n-C_4F_9)$_2$·2THF in d_8-THF; ^{19}F resonance frequency = 282.35 MHz, no decoupling during acquisition. The 1D ^{19}F and ^{13}C{^{19}F} DEPT 135 spectra are given along the corresponding axes. The positive amplitude characterizes the ^{13}C signal (A) of the CF_3 group.

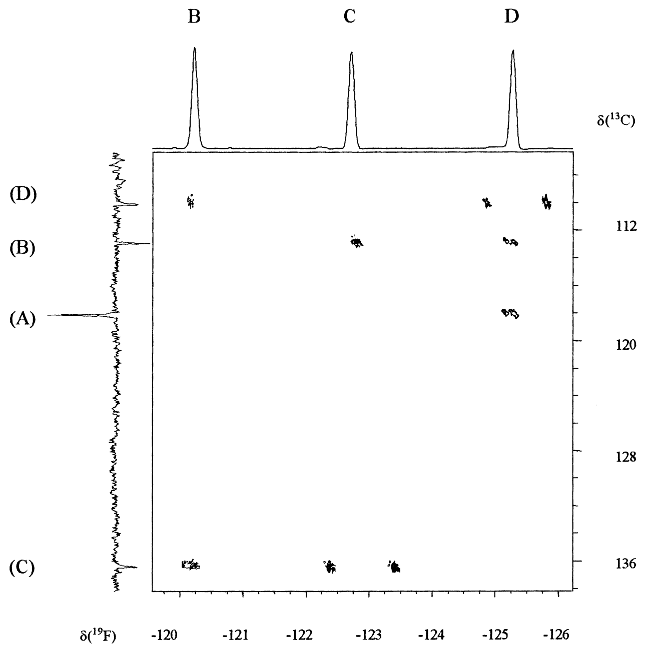


Fig. 3. ^{19}F detected (CF_2 groups only) ^2J-^{13}C, ^{19}F correlated NMR (HMQC) spectrum of Zn(n-C_4F_9)$_2$·2THF in d_8-THF; ^{19}F resonance frequency = 282.35 MHz, no decoupling during acquisition. The 1D ^{19}F and ^{13}C{^{19}F} DEPT 135 spectra are given along the corresponding axes.

been used to characterize the fluorine atoms bound to the α carbon atom. Furthermore, the ^{13}C{^{19}F} DEPT 135 spectrum (given along the ^{13}C axis of the 2D spectrum, Fig. 2) characterizes the ^{13}C signal of the CF_3 group by its opposite phase with respect to those of the CF_2 group signals. The ^1J-^{13}C, ^{19}F correlation spectrum obtained from Zn(n-C_4F_9)$_2$·2THF (correlation of the ^{13}C resonances with the ^{19}F signals of the CF_2 groups, Fig. 2) shows that the low field carbon signal is connected to signal C in the ^{19}F spectrum. Consequently, these two signals must be assigned to the C^1F_2 group. This also leads to the assignment of signal D to the C^3F_2 group. Therefore, the weak cross peak between A and C in the ^{19}F COSY spectrum is not caused by a ^3J but by a ^5J(^{19}F, ^{19}F) coupling. Since all ^{19}F signals have now been assigned the remaining peaks of the ^1J-^{13}C, ^{19}F correlation spectrum can be used in signal assignment of the ^{13}C spectrum (see Table 2). ^{19}F and ^{13}C signals belonging to the same CF_n group are labeled by the same letters, those of the ^{13}C signals are given in parentheses.

If in addition to ^1J also ^2J correlations are observed, ^{13}C, ^{19}F correlation spectroscopy provides the complete information on the constitution of a perfluoroalkyl group. This is a consequence of the relation $^1J(^{13}C,^{19}F) \gg {}^2J(^{13}C,^{19}F) \gg {}^3J(^{13}C,^{19}F)$ and the simple conclusion that the ^1J correlation F-C^1 and the ^2J correlation F-(C^1)-C^2 also establishes the direct neighborhood of the groups C^1F_2-$C^2F_{2/3}$. It should be mentioned that this is a unique feature of perfluorinated alkanes or alkyl groups since the relation mentioned above does not hold for partly fluorinated alkyl groups. Also in the case of other elements, the carbon couplings situation is more complex. For instance, the constitutional analysis of hydrocarbons is complicated by the fact that ^2J(^{13}C, ^{1}H) may be of the same order of magnitude as ^{13}C, ^{1}H couplings over more than two bonds.

The constitutional analysis by ^{13}C, ^{19}F correlations over one and two bonds will be demonstrated by the example of Zn(n-C_4F_9)$_2$·2THF. In addition to the ^1J correlation (Fig. 2) Fig. 3 shows the ^2J-^{13}C, ^{19}F correlated spectrum of this compound (the ^{13}C spectrum is correlated to the ^{19}F signals of the CF_2 groups only). Signal labeling in the ^{13}C spectrum (identical letters for ^{19}F and ^{13}C signals belonging to the same CF_x group) has been adopted from the ^1J correlation spectrum. The ^1J cross peaks D/(D) and C/(C) could not be suppressed by the HMQC pulse sequence (see Section 2) of the ^2J correlation but are clearly characterized by the strong splitting along the ^{19}F axis. From the ^2J cross peaks the connectivities (A)/D, D/(B), and (B)/C can be deduced. Since A has already been assigned to the CF_3 group the connectivities of the ^2J correlation directly establish the constitution of a perfluorobutyl group (A–D–B–C) confirming the signal assignment given in the first line of Scheme 1.

3.2. Bis(tridecafluorohexyl)zinc Zn(n-C_6F_{13})$_2$·2THF

The ^{19}F, ^{19}F COSY spectrum of Zn(n-C_6F_{13})$_2$·2THF (Fig. 4) shows the strong cross peaks B/E and E/A as well as F/C and C/D. Since these peaks correspond to ^4J couplings they indicate the connectivities B–O–E–O–A and F–O–C–O–D. From its chemical shift and relative intensity A can be attributed to the CF_3 group and consequently an

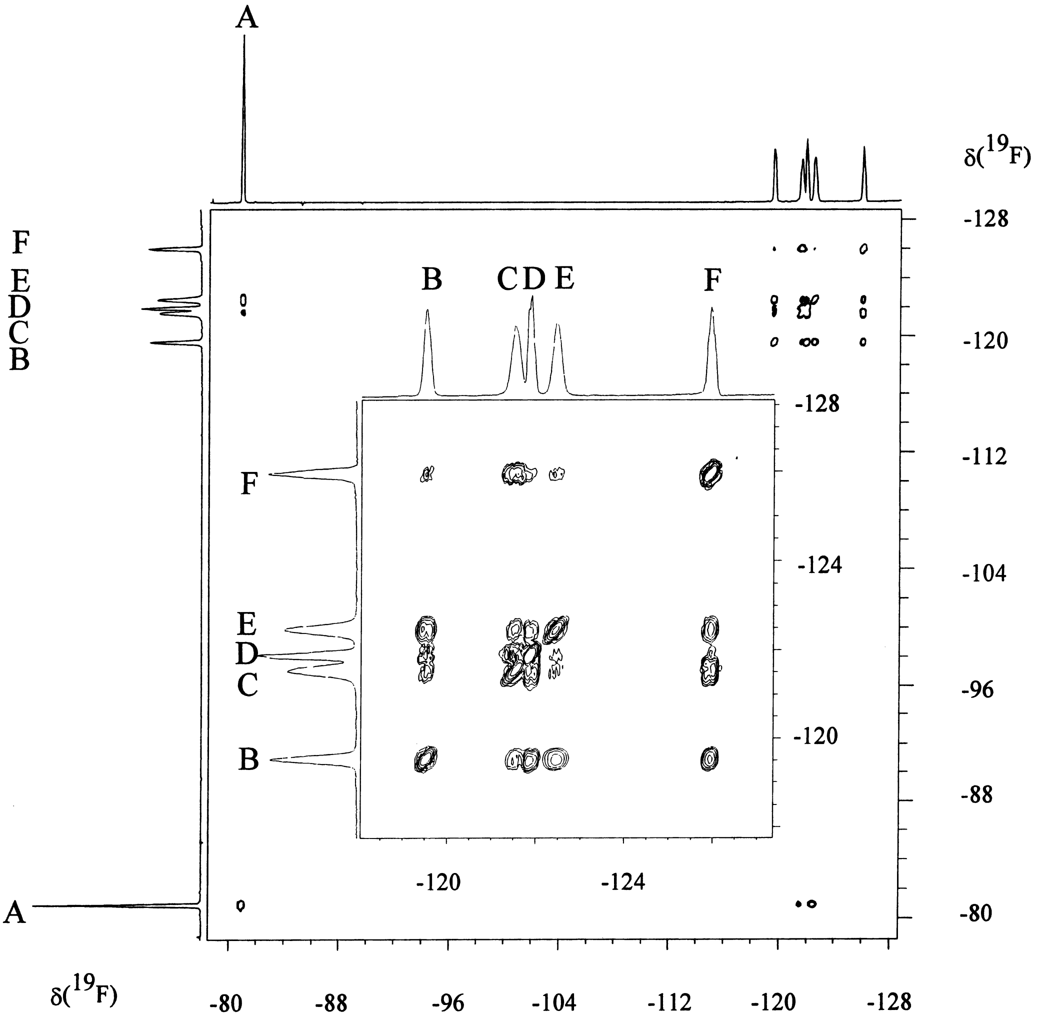
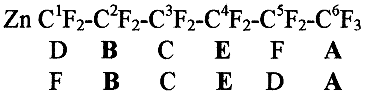


Fig. 4. 188.13 MHz ^{19}F COSY spectrum of Zn(n-C_6F_{13})$_2$·2THF in d_8-THF. The expanded region of the CF_2 groups is shown in the centre of the 2D map.

unambiguous assignment of the connectivity B–O–E–O–A to the perfluorohexyl group becomes possible. In contrast to that, two different assignments of the sequence F–O–C–O–D are possible (see Scheme 2).

Although, additional cross peaks resulting from ^3J and/or long range couplings are present in the COSY spectrum none of them can be used to eliminate the remaining uncertainty. The CF_3 group (A) shows an additional cross peak with C (via five bonds) but none with D or F, whereas B is connected with both D and F by weak cross peaks. Thus, as in the analysis of the ^{19}F, ^{19}F COSY spectrum of Zn(n-C_4F_9)$_2$·2THF at least one additional item of information is needed to achieve complete assignment.



$$\begin{array}{lcccccc} \mathrm{Zn} & \mathrm{C^1F_2}\text{-} & \mathrm{C^2F_2}\text{-} & \mathrm{C^3F_2}\text{-} & \mathrm{C^4F_2}\text{-} & \mathrm{C^5F_2}\text{-} & \mathrm{C^6F_3} \\ & \mathrm{D} & \mathbf{B} & \mathrm{C} & \mathrm{E} & \mathrm{F} & \mathrm{A} \\ & \mathrm{F} & \mathbf{B} & \mathrm{C} & \mathrm{E} & \mathrm{D} & \mathrm{A} \end{array}$$

Scheme 2.

As described before, the missing information is available from the single bond ^{13}C, ^{19}F correlated spectrum (Fig. 5). It clearly demonstrates that D is connected with the ^{13}C signal of C^1, which shows the characteristic downfield shift of the metal bonded carbon atom. This unambiguously confirms the assignment given in line one of Scheme 2. The remaining cross peaks of the spectrum have been used in the assignment of the other ^{13}C signals (Table 2). Although, the ^{13}C signal of the CF_3 group is characterized by the phase relations of the DEPT 135 spectrum (given along the ^{13}C axis of the 2D spectrum in Fig. 5) the correlation A/(A) was confirmed by an independent experiment.

3.3. Bis(tridecafluorohexyl)zinc Zn(n-C_6F_{13})$_2$·$2CH_3CN$

The substitution of tetrahydrofuran as donor ligand and solvent by acetonitrile clearly influences the ^{19}F chemical shifts (see Table 2). Although, the sequence of the δ values $C^6F_3 \gg C^2F_2 > C^3F_2 > C^4F_2 > C^5F_2$ is not altered, the signal of the C^1F_2 group experiences a considerable highfield

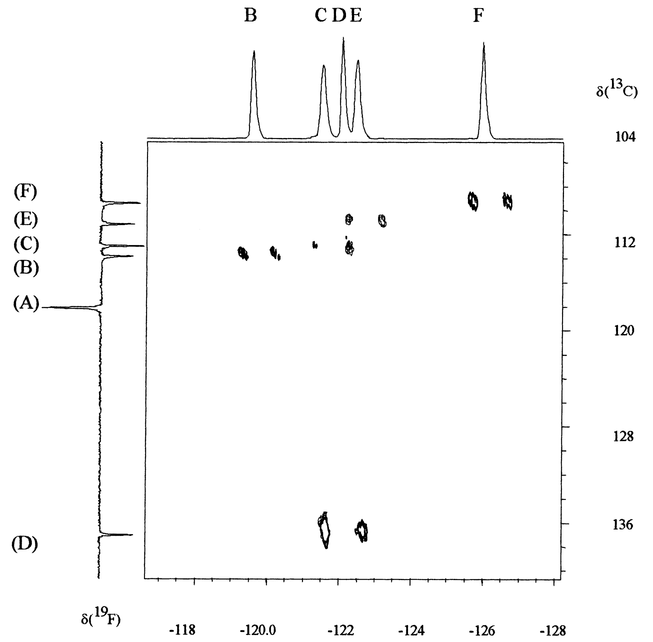


Fig. 5. ^{19}F detected (CF_2 groups only) ^1J-^{13}C, ^{19}F correlated NMR (HMQC) spectrum of $Zn(n\text{-}C_6F_{13})_2 \cdot 2THF$ in d_8-THF; ^{19}F resonance frequency = 282.35 MHz, no decoupling during acquisition. The 1D ^{19}F and $^{13}C\{^{19}F\}$ DEPT 135 spectra are given along the corresponding axes. The positive amplitude characterizes the ^{13}C signal (A) of the CF_3 group.

shift moving from a position between the signals of the C^3F_2 and C^4F_2 group (in THF) to a position between the signals of the C^4F_2 and C^5F_2 group (in acetonitrile). Thus, signal assignment in the spectrum obtained with THF as a solvent cannot be transferred to the spectrum acquired from a solution in acetonitrile. Instead, a separate ^{19}F, ^{19}F COSY experiment had to be carried out which provided the assignments given in Table 2.

$\mathrm{Zn\ C^1F_2\text{-}C^2F_2\text{-}C^3F_2\text{-}C^4F_2\text{-}C^5F_2\text{-}C^6F_2\text{-}C^7F_3}$
E B C D F G A
E G C D F B A

Scheme 3.

3.4. *Bis(pentadecafluoroheptyl)zinc $Zn(n\text{-}C_7F_{15})_2 \cdot 2THF$*

The ^{19}F NMR spectrum of $Zn(n\text{-}C_7F_{15})_2 \cdot 2THF$ shows seven separate signals, which were labeled A to G from low to high field. From the strong cross peaks (corresponding to $^4J(^{19}F, ^{19}F)$ coupling) in the homonuclear COSY spectrum (Fig. 6) two independent sequences of connectivities can be established. The first one is A/F, F/C and C/E and the second one G/D and D/B. Since A, according to its strong downfield shift and its relative intensity, can be assigned to the CF_3 group the assignment of the signals connected with A: F, C and E is straightforward (see Scheme 3).

In contrast to that, G and B of the sequence G, D, B may be assigned in two different ways. In general, weak cross peaks corresponding to ^3J or ^5J (or even ^6J) coupling may help to overcome the resulting ambiguity; but also in this case they do not. In accordance with the safe assignment of

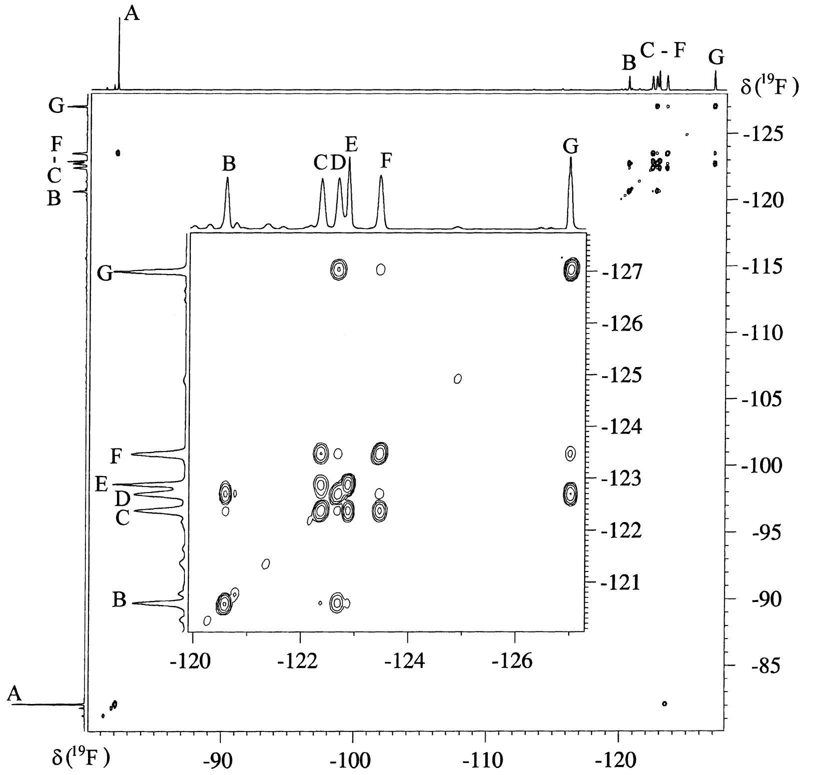


Fig. 6. 470.59 MHz ^{19}F COSY spectrum of $Zn(n\text{-}C_7F_{15})_2 \cdot 2THF$ in d_8-THF. The expanded region of the CF_2 groups is presented in the centre of the 2D map.

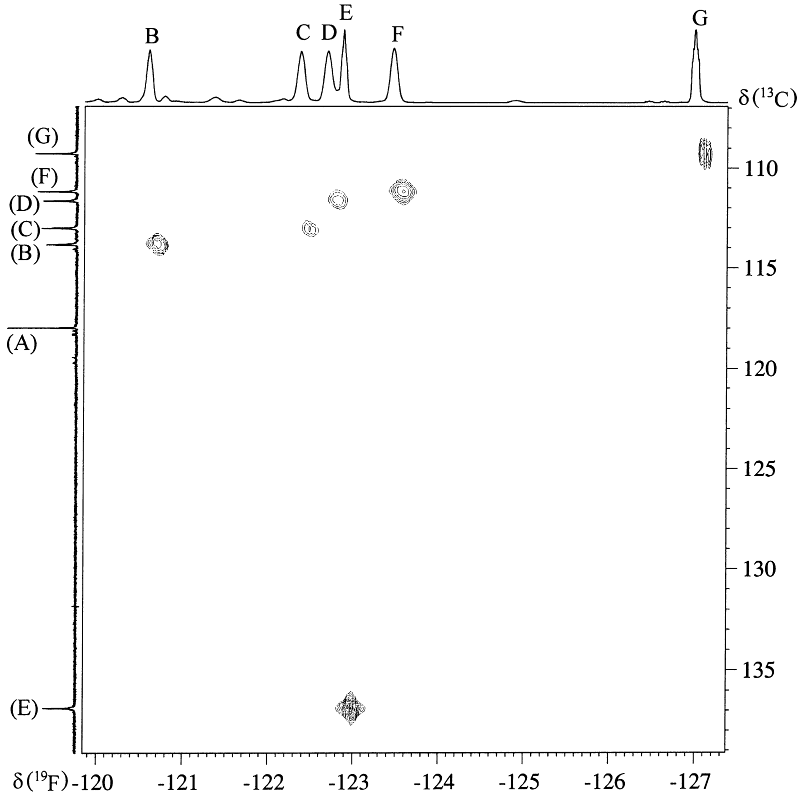


Fig. 7. ^{19}F detected (CF_2 groups only) ^{1}J-^{13}C, ^{19}F correlated NMR (HMQC) spectrum of $Zn(n\text{-}C_7F_{15})_2{\cdot}2THF$ in d_8-THF; ^{19}F resonance frequency = 470.59 MHz; ^{13}C decoupling during acquisition. The 1D ^{19}F and ^{13}C spectra are given along the corresponding axes; signal (A) corresponds to the CF_3 group. Note that the shift difference between 1D and 2D peaks along the ^{19}F axes corresponds to the isotopic effect of ^{13}C on the ^{19}F resonance.

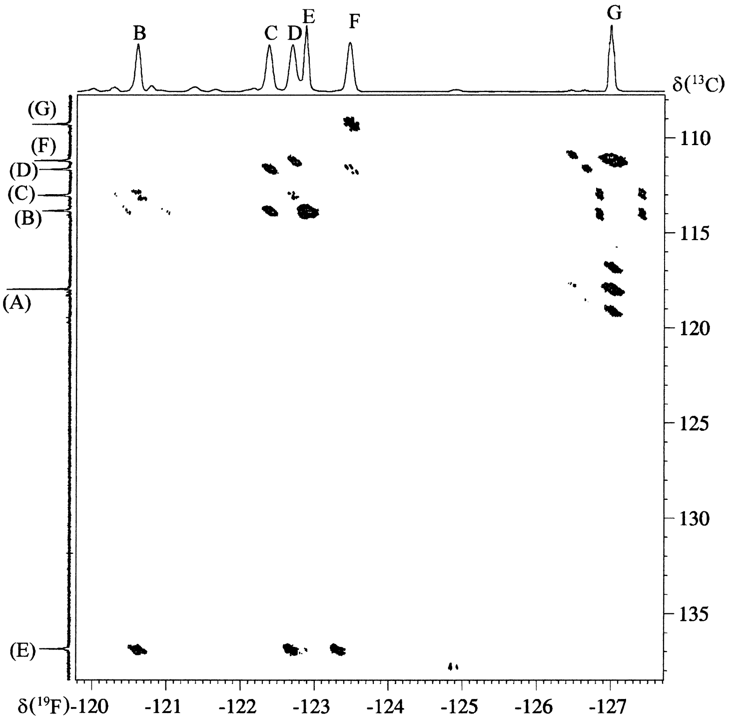


Fig. 8. ^{19}F detected (CF_2 groups only) ^{2}J-^{13}C, ^{19}F correlated NMR (HMQC) spectrum of $Zn(n\text{-}C_7F_{15})_2{\cdot}2THF$ in d_8-THF; ^{19}F resonance frequency = 470.59 MHz, no decoupling during acquisition. The 1D ^{19}F and ^{13}C spectra are given along the corresponding axes. The 'triplet' of the cross peak G/(A) is due to a distorted line shape of the strong central peak. Two impurities showing ^{19}F resonances downfield of G also cause strong ^{2}J cross peaks.

C, D and F the weak cross peaks F/D and C/D correspond to interactions via three bonds. The remaining cross peaks F/G and C/B also do not answer the open question, since they may either result from ^{3}J or ^{5}J couplings, which are in agreement with both of the possible assignments of B and G. Unfortunately, also ^{1}J-^{13}C, ^{19}F correlation cannot help to solve the problem since this experiment only aids in the identification of the α-$C^{1}F_2$ group, which has already been assigned to signal E. Thus, the only way to achieve a complete assignment is to carry out both, ^{1}J- and ^{2}J-^{13}C, ^{19}F correlation.

The ^{1}J-^{13}C, ^{19}F HMQC spectrum (Fig. 7) correlates the ^{19}F and ^{13}C signals that belong to the same $CF_{2/3}$ group. Thus, ^{19}F and ^{13}C signals originating from the same $CF_{2/3}$ group have been labeled by identical letters, those of the ^{13}C signals are given in parentheses. Making use of these labels deduced in the ^{1}J-^{13}C, ^{19}F HMQC spectrum, the sequence of adjacent $CF_{2/3}$ groups can easily be determined from the cross peaks of the ^{2}J-correlated spectrum (Fig. 8). Starting from the ^{13}C signal (A) of the $C^{7}F_3$ group we come to the ^{19}F signal G, which must belong to the neighboring $C^{6}F_2$ group. From there we proceed (via the second cross peak of G) to the ^{13}C signal (F) and from there (via the second cross peak of (F)) to the ^{19}F signal D. At this point the connectivities (A) ⇒ G ⇒ (F) ⇒ D have been deduced. Continuing in the same way the complete sequence (A) ⇒ G ⇒ (F) ⇒ D ⇒ (C) ⇒ B ⇒ (E) is established. This finding confirms the result of the ^{19}F, ^{19}F COSY spectrum and additionally gives the correct assignment of the signals B and G.

3.5. *Bis(heptadecafluorooctyl)zinc Zn(n-C_8F_{17})$_2$·2THF*

Two of the CF_2 groups of Zn(n-C_8F_{17})$_2$·2THF show overlapping ^{19}F signals (D and E). However, the corresponding cross peaks D/G, D/B as well as E/H, E/C of the ^{19}F COSY spectrum (Fig. 9) are well separated from each other and allow for an accurate determination of δ(D) and δ(E). Thus, all peaks of the COSY spectrum are well resolved so that the following two sequences of intense cross peaks were identified: A/G, G/D, D/B as well as H/E, E/C, C/F. Consequently, ^{4}J coupling connects the signals A–G–D–B and H–E–C–F. Since A corresponds to the CF_3 group (chemical shift and relative intensity of A) the assignment of the first sequence of signals to the perfluorooctyl group is clear, whereas two different possibilities remain for the second sequence (Scheme 4).

Zn $C^{1}F_2$-$C^{2}F_2$-$C^{3}F_2$-$C^{4}F_2$-$C^{5}F_2$-$C^{6}F_2$- $C^{7}F_2$-$C^{8}F_3$
F **B** C **D** E **G** H **A**
H **B** E **D** C **G** F **A**

Scheme 4.

In addition to the strong cross peaks only two connectivities resulting from weak couplings were detected: H/G and B/F. However, for the first time both connectivities are

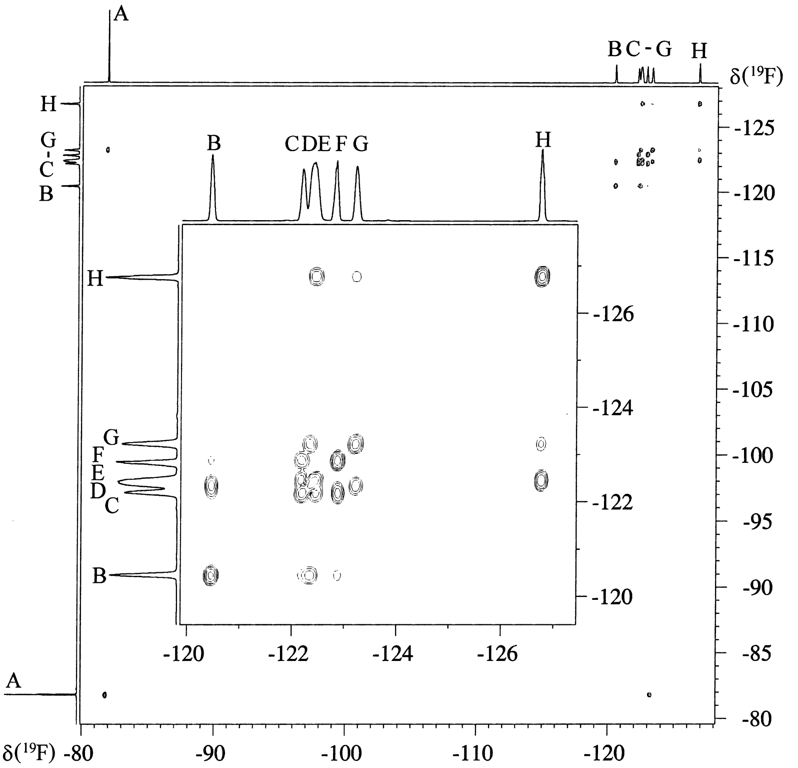


Fig. 9. 470.59 MHz ^{19}F COSY spectrum of Zn(n-C_8F_{17})$_2$·2THF in d_8-THF. The expanded region of the CF_2 groups is shown in the centre of the 2D map.

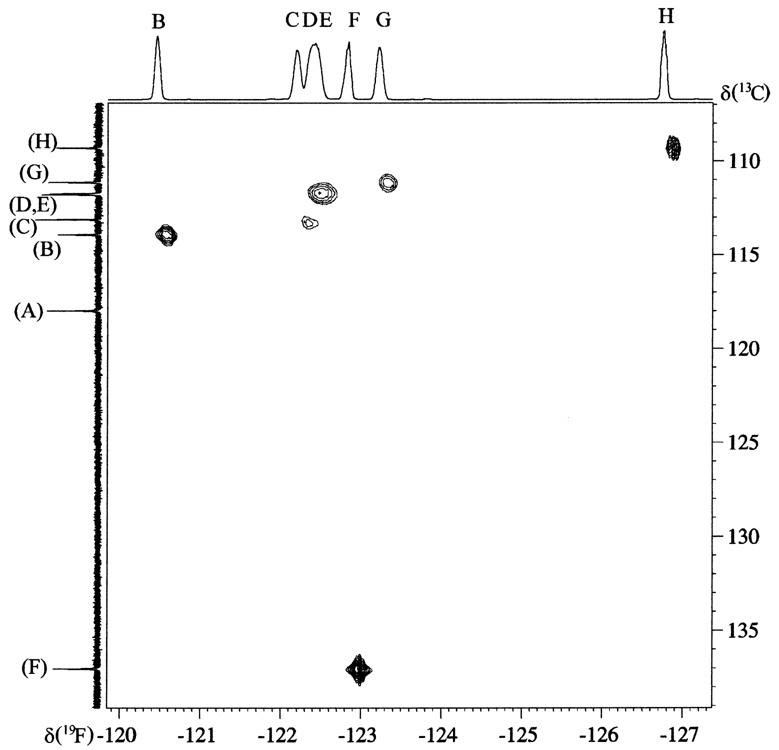


Fig. 10. ^{19}F detected (CF_2 groups only) ^{1}J–^{13}C, ^{19}F correlated NMR (HMQC) spectrum of Zn(n-C_8F_{17})$_2$. 2 THF in d$_8$-THF; ^{19}F resonance frequency = 470.59 MHz; ^{13}C decoupling during acquisition. The 1D ^{19}F and ^{13}C spectra are given along the corresponding axes; signal (A) corresponds to the CF_3 group.

significant. Considering the assignment given in the first row they would both correspond to ^{3}J couplings, which is in agreement with expectation. In contrast to that, detectable ^{7}J couplings must be assumed, if the second assignment is correct. Thus, the cross peaks H/G and B/F only match the first alternative. In consequence of this, for the first time complete assignment of all ^{19}F signals has been achieved by the homonuclear COSY spectrum. Concomitantly, this assignment proves the constitution of the n-perfluorooctyl group since it is only compatible with an unbranched chain of seven CF_2 groups terminated by a CF_3 group. The assignment of the ^{13}C signals (Table 2) was carried out by a ^{1}J-^{13}C, ^{19}F correlation (Fig. 10).

3.6. Chemical shifts

The ^{19}F and ^{13}C chemical shifts of the bis(perfluoroalkyl)zinc compounds Zn(n-C_mF_{2m+1})$_2$·2D (D = THF, $m = 4$, 6, 7, 8; D = CH_3CN, $m = 6$) are summarized in Table 2. The ^{19}F signal of the CF_3 group and the ^{13}C signal of the zinc substituted CF_2 group (C^1F_2), both appearing at the low field side of the corresponding spectra, show characteristic shift

Table 2
^{19}F and ^{13}C chemical shifts of the bis(perfluoroalkyl)zinc compounds (^{19}F chemical shifts are characterized by a negative sign)[a]

Compound	Solvent	C^1F_2	C^2F_2	C^3F_2	C^4F_2	C^5F_2	C^6F_2	C^7F_2	CF_3
Zn(n-C_4F_9)$_2$·2THF	d$_8$-THF	−122.3	−120.2	−125.5					−80.9
		136.4	112.9	110.2					118.1
Zn(n-C_6F_{13})$_2$·2THF	d$_8$-THF	−121.9	−119.5	−121.5	−122.5	−125.9			−80.9
		137.1	113.9	113.0	111.2	109.5			118.2
Zn(n-C_6F_{13})$_2$·2CH_3CN	CD_3CN	−124.8	−122.0	−122.3	−123.2	−126.5			−81.2
		137.0	114.5	113.1	111.1	109.2			117.8
Zn(n-C_7F_{15})$_2$·2THF	d$_8$-THF	−122.9	−120.6	−122.4	−122.7	−123.5	−127.0		−82.1
		136.9	113.8	113.0	111.6	111.2	109.3		118.0
Zn(n-C_8F_{17})$_2$·2THF	d$_8$-THF	−122.8	−120.5	−122.2	−122.4	−122.4	−123.2	−126.8	−81.8
		137.1	114.0	113.2	111.8	111.7	111.2	109.3	118.0

[a] Chemical shifts values are given in ppm with respect to trichlorofluoromethane (^{19}F) and tetramethylsilane (^{13}C) as reference compounds and have been measured indirectly relative to the deuterium signal of the solvent.

values. Thus, as has been shown before, they play an important role in spectra interpretation. Furthermore, the C^qF_2 groups of all perfluoroalkyl ligands show an interesting trend of ^{13}C chemical shifts. They are shifted to smaller δ values (higher field) with increasing values of q. This corresponds to the influence of the zinc atom causing a low field shift, which is strong at the α carbon (19 ppm) intermediate at the β-carbon (5 ppm) and small at the γ-carbon (1.9 ppm). At the other end of the chain the CF_3 group shows a strong α-effect shifting to highfield (−9 ppm) but a moderate β-effect (2.1 ppm) and a very weak γ-effect (0.6 ppm) in the opposite direction. Thus, signals of C^qF_2 groups in the middle of the chain fall into a very narrow region and may overlap if the total chain length is larger than seven. Nevertheless, in the case of $Zn(n\text{-}C_8F_{17})_2\cdot 2THF$ the signals of C^4 and C^5 could be resolved and were found to show the expected order: C^4 downfield of C^5. Consequently, the sequence of the C^qF_2 group in the ^{13}C spectrum indicates their position in the perfluoroalkyl chain. The signal of the CF_3 group does not spoil this information since it always appears at the characteristic position at about 118.8 ppm (between the signal of C^1F_2 and C^2F_2) and may additionally be characterized by a $^{13}C\{^{19}F\}$ DEPT 135 spectrum.

A similar trend is found in the ^{19}F spectrum. Here, a highfield shift of consecutive C^qF_2 segments starts with the C^2F_2 group. Unfortunately, the signal of the C^1F_2 group appears at a not well defined position (−125.5 to −121.9 ppm) disturbing this sequence. Although, the line width of the C^1F_2 signal is not as broad as those of the other C^qF_2 groups a safe identification is only possible by ^1J-^{13}C, ^{19}F correlation (or by other two-dimensional experiments). Thus, unambiguous assignment of the C^qF_2 groups requires the application of two-dimensional methods.

When the donor ligand and the solvent are changed from THF (d_8-THF) to CH_3CN (CD_3CN) all ^{19}F chemical shifts of $Zn(n\text{-}C_6F_{13})_2\cdot 2D$ experience a highfield shift, whereas the ^{13}C shifts practically remain unchanged. The strongest effect results for the $\delta(^{19}F)$ value of the C^1F_2 group, which corresponds to its direct vicinity to the center of ligand exchange (Fig. 10).

4. Conclusion

In consequence of the condition $^4J(^{19}F, ^{19}F) > {}^3J(^{19}F, ^{19}F) \cong {}^5J(^{19}F, ^{19}F)$ homonuclear ^{19}F, ^{19}F COSY spectra of n-perfluoroalkyl groups deliver two separate sequences of connectivities. In the case of a perfluorohexyl group showing six different ^{19}F signals A–F the connectivities **B**–O–**E**–O–**A** and F–O–C–O–D have been found (see Scheme 2). Since the signal of the terminal CF_3 group (in our example A) can always be identified (shift and relative intensity) there exist two different possibilities to put the sequences together; in our example: F–**B**–C–**E**–D–**A** or D–**B**–C–**E**–F–**A**. In order to find the correct connectivity different strategies can be applied.

1. Low intensity cross peaks resulting from ^3J, ^5J or even ^6J couplings may be examined. Since the source of these cross peaks is uncertain, they scarcely help to solve the problem, but rather confirm that the two sequences belong to the same molecule.
2. For perfluoroalkyl groups with an even number of carbon atoms the metal substituted CF_2 group (in our example F or D) and the CF_3 group (A) are in different basic sequences. In this case ^1J-^{13}C, ^{19}F correlation will solve the problem since the metal substituted carbon atom shows a characteristic low field shift identifying the terminal CF_2 group.
3. In any case the combination of a ^1J- and ^2J-^{13}C, ^{19}F correlated spectrum will give the connectivity of all CF_x groups. This results from the fact that ^1J correlation $^{19}F_x$-$^{13}C^q$ in combination with ^2J correlation $^{19}F_x$-$^{13}C^q$-$^{13}C^{q+1}$ also establishes the connectivity F_x-$^{13}C^q$–$C^{q+1}F_x$. Although very effective, this method is most time consuming.

Applying method (1) it is helpful to consider that CF_3 groups usually do not show any cross peaks resulting from homonuclear ^3J coupling.

Finally, it can be stated that the constitution of the perfluoroalkyl groups of the zinc complexes $Zn(n\text{-}C_mF_{2m+1})_2\cdot 2D$ ($D = THF$, $m = 4, 6, 7, 8$; $D = CH_3CN$, $m = 6$) has been unambiguously established by two-dimensional ^{19}F, ^{19}F and ^{19}F, ^{13}C correlation NMR spectroscopy. The results clearly confirm the structures, which have been claimed earlier in a paper [15] describing the synthesis of these compounds.

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