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Synthesis and characterization of tin tetrafluoride adducts with fluoroalkyl phosphoryl ligands

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ABSTRACT

The reaction of SnF_4 with $(\text{R}_2\text{N})_n\text{P}(\text{O})(\text{OCH}_2\text{CF}_3)_{3-n}$ (n = 0-2) produces a series of new octahedral complexes of SnF_4L_2 type (L = $(\text{R}_2\text{N})_2\text{P}(\text{O})(\text{OCH}_2\text{CF}_3)$; R = Me (1); Et (2), L = $\text{R}_2\text{NP}(\text{O})(\text{OCH}_2\text{CF}_3)_2$; R = Me (3); Et (4) or L = $P(\text{O})(\text{OCH}_2\text{CF}_3)_3$ (5)). The adducts have been characterized by multinuclear (^{19}F , ^{31}P and ^{119}Sn) NMR, IR spectroscopy and elemental analyses. The NMR data particularly the ^{19}F NMR spectra show the existence of complexes as mixtures of *cis* and *trans* isomers. The variable temperature NMR study in CH₂Cl₂ solutions in the presence of excess ligand indicated that the ligand exchange at room temperature is slow for 1–4 and fast only for 5. The results were compared with those of SnCl₄ analogues and show the formation of higher *trans* ratios for the studied complexes.

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1. Introduction

Octahedral tin(IV) complexes of the general formula SnX_4L_2 (X = halide and L is the phosphoryl ligand), readily accessible via reaction between SnX_4 and various neutral donor ligands, have attracted much interest [1–4]. For instance, an extensive coordination chemistry has been devoted to tin(IV) chloride and bromide [5–11]. Although it was reported that the Lewis acidity of the four SnX_4 is greatest for SnF_4 [12], and despite the very different electronic properties conferred on the metal by the hard, small electronegative fluoride, the coordination chemistry of SnF_4 is still much less studied compared to the other tin halides (X = Cl, Br or I) [12–15].

In a previous work, we reported a systematic study of the complexes of SnCl₄ with the ligands $(R_2N)_nP(O)(OCH_2CF_3)_{3-n}$ and found that the *trans* isomer dominates the chemistry [16–18]. More recently, we have shown that the use of complexes of the harder SnF₄ Lewis acid with $(R_2N)_nP(O)F_{3-n}$ led to higher formation rates of the *trans* complex even with the weaker Lewis bases $R_2NP(O)F_2$ [19] compared to corresponding SnCl₄ analogues [16,17]. Herein, we report the synthesis and spectroscopic characterization of a new series of SnF₄ complexes with $(R_2N)_2P(O)OCH_2CF_3$, $R_2NP(O)(OCH_2CF_3)_2$, and $(CF_3CH_2O)_3PO$ and show again the importance of using ¹⁹F NMR spectroscopy to easily assign the *trans* and *cis* isomers of such complexes even at room temperature.

2. Results and discussion

2.1. Synthesis

Anhydrous SnF₄ has a polymeric sheet structure [20] and is therefore unreactive towards neutral ligands. A convenient method for the synthesis of its complexes is provided by SnF₄(MeCN)₂ made from SnF₂, I₂ and MeCN as described by Tudela and co-workers [21,22]. Treatment of SnF₄(MeCN)₂ in anhydrous dichloromethane solution with (R₂N)₂P(O)OCH₂CF₃, R₂NP(O)(OCH₂CF₃)₂ (R = Me or Et), or (CF₃CH₂O)₃PO gives white solids with the composition SnF₄L₂ (L = phosphoryl ligand) in moderate to good yields. The solids are moderately soluble in dichloromethane and chloroform with (CF₃CH₂O)₃P(O) adduct being poorly soluble. They are, in general, much less soluble in these solvents than their SnCl₄ analogues.

2.2. Spectroscopic studies

The strong bands observed in the infrared spectra within the range 1200–1210 cm⁻¹ for **1** and **2** and 1240–1260 cm⁻¹ for **3–5** are assigned to ν (P=O) stretching vibrations. These are shifted towards lower wave numbers compared to those of the free ligands. The coordination shift is consistent with phosphoryl coordination to the tin atom. This shift is 32, 78 and 85 cm⁻¹ for **5**, **1** and SnF₄[(Me₂N)₃PO]₂ [19], respectively, reflecting a difference in the basicity strength between the ligands in these complexes. This is most probably due to the nature of the substituents on the phosphorus atom in these ligands (i.e. due to difference in the electronegativities of nitrogen and oxygen atoms linked directly to

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1	6

Table 1					
NMR data	$(\delta/\text{ppm and})$	I/Hz) for the	e complexes	[SnF4L2] in	n CD ₂ Cl ₂

Ligand (L)		³¹ P	¹⁹ F	¹¹⁹ Sn	¹ J _{Sn-F}	² J _{Sn-P}	$^{2}J_{F-F}$
$(Me_2N)_2P(O)OCH_2CF_3$	cis trans	20.39 19.18	-75.6(t), -151(t), -162(t) -75.7(t), -154(t)	$-648 \\ -652$	_ 1711	16.8 36.3	53.6 -
$(Et_2N)_2P(O)OCH_2CF_3$	cis trans	16.70 15.84	-76.2(t), -150(t),-159(t) -76.3(t), -153(t)	-652 -659	1700	26.8 50.3	53.6 -
$Me_2NP(O)(OCH_2CF_3)_2$	cis trans	5.95 6.40	-76.07(t), -151(t),-163(t) -76.04(t), -153(s)	-647 -650	1965 1754	-	56.5 -
$Et_2NP(O)(OCH_2CF_3)_2$	cis trans	5.06 4.68	-76.4(t), -151(t), -163(t) -76.5(t), -153(s)	-648 -651	1965 1754	43.1	55.0 -
$P(O)(OCH_2CF_3)_3^a$	cis trans	-5.27 -4.98	-76.2(t),-149(t), -164(t) -77.8(d), -151(s)	$-649 \\ -652$	2016 1790	-	57.9 _

^a At 218 K.

the phosphorus atom of the ligand). A strong absorption band at $570-590 \text{ cm}^{-1}$ with two to three much weaker bands in the region $575-615 \text{ cm}^{-1}$ are also observed in the IR spectra of these complexes in the solid state and correspond to the stretching vibration of the Sn–F bond. In chloroform solution, the intensity of the bands at $575-615 \text{ cm}^{-1}$ is relatively raised but remains weak when compared to that at $570-590 \text{ cm}^{-1}$. In addition, the latter band becomes broad and two bands may coalesce within a wider envelope especially for complex **5**. Such a behaviour could be attributable to a mixture of the *cis* isomer, which would be expected to show two to four bands in the tin–halogen stretching region, and the *trans* isomer, which should show only one [23] with the latter form predominating. This is in good agreement with our solution NMR data shown below.

The NMR spectra of the complexes were recorded in dichloromethane solutions and the data show the presence of both *cis* and *trans* isomers (Table 1). The approximate isomer ratio was determined from the ¹⁹F{¹H} NMR spectra. Whilst the *trans* isomer predominates in complexes **1–4**, the *cis* form is the major isomer in complex **5**. Despite the fact that resonances were observed at ambient temperatures in the ³¹P, ¹⁹F and ¹¹⁹Sn NMR spectra of complexes **1–4**, the corresponding spectra of complex **5** showed broad and poorly resolved features and the solutions were cooled to 218 K to improve resolution.

The ³¹P NMR spectra display a singlet resonance for each isomer with similar chemical shifts and weak ^{117/119}Sn satellites. The ¹⁹F NMR spectra are more useful and show, in the SnF₄ region, singlet resonances for the *trans* isomers and two triplets for the *cis* with clearly resolved ¹J(¹¹⁹Sn-¹⁹F) and ¹J(¹¹⁷Sn-¹⁹F) (Fig. 1). The ¹⁹F spectra also show, in the region of the ligand fluorine atoms, two triplets for the *cis* and *trans* isomers due to ${}^{3}J(H-F)$ couplings.

Interestingly, the corresponding ¹¹⁹Sn NMR spectra show also the presence of both *cis* and *trans* isomers. This was observed at ambient temperatures for **1–4** as a symmetrical quintet of triplets for the *trans* isomer and a multiplet (t,t,t) for the *cis* isomer (Fig. 2) with coupling constants consistent with those deduced from the ¹⁹F{¹H} and ³¹P{¹H} spectra. These data are in good agreement with those obtained for related complexes [12]. For complex **5**, the ¹¹⁹Sn resonances are broad and ill-defined at ambient temperatures but on cooling the samples at 218 K, the resonances sharpen and split giving defined features with predominance of the multiplet related to the *cis* isomer. However, the quality of the ¹¹⁹Sn NMR spectrum of **5** was lower than those of **1–4** due to poor solubility of this complex. The above results are in good agreement with our previously reported data on corresponding (R₂N)_nP(O)F_{3–n} complexes [19].

We have previously shown that $SnCl_4$ complexes with $(R_2N)_nP(O)(OCH_2CF_3)_{3-n}$ are labile in solution with a fast ligand exchange at room temperature; cooling the samples was necessary to observe sharp resonances and resolved couplings [18]. This was compared with the solution behaviour of the corresponding SnF_4 analogues, **1–5**, in the presence of an excess of ligand. The ³¹P and ¹⁹F NMR spectra of these solutions display for complexes **1–4** separate signals for free, *cis* and *trans* ligands, showing that no ligand exchange is occurring at room temperature in these complexes (Fig. 3). However, the solution spectra of **5** show at room temperature average signals which broaden and split on cooling and give at 218 K separate signals for free, *cis* and *trans*



-148 -149 -150 -151 -152 -153 -154 -155 -156 -157 -158 -159 -160 -161 -162 -163 -164 ppm

Fig. 1. SnF₄ region of the ¹⁹F-{¹H} NMR spectrum of 1 in CD₂Cl₂ at 298 K (*: ^{119/117}Sn satellites in the *trans* isomer).



24 23 22 21 20 19 18 17 16 15 14 13 12 11 ppm

Fig. 3. ³¹P-{¹H} NMR spectrum of **2** in the presence of excess ligand in CD₂Cl₂ at 298 K (L_F, L_{cis} and L_{trans} indicate the ligand in the free, *cis* and *trans* positions, respectively; *: ^{119/} ¹¹⁷Sn satellites).

ligands. This indicates that ligand exchange at room temperature is slow on the NMR time scale for **1–4** and only fast for complex **5**, in contrast to SnF_4 complexes with $(R_2N)_2P(O)F$ and $R_2NP(O)F_2$ which all show fast ligand exchange at room temperature [19]. Comparison of *cis* and *trans* ratios with those obtained for $SnF_4[(Me_2N)_3PO]_2$ [19], $SnF_4(Me_3PO)_2$ and $SnF_4(Ph_3PO)_2$ [12] suggests that the donor power of the ligands Me_3PO and $(Me_2N)_3PO$ are similar to that of $(Me_2N)_2P(O)OCH_2CF_3$, while the ligands Ph_3PO and $Me_2NP(O)(OCH_2CF_3)_2$ form similar *cis:trans* ratios showing nearly identical donor power (Table 2).

In addition, examination of Table 2 shows, for each tin halide, that higher *cis* ratios are obtained as the substituents on the phosphorus atom become more electronegative, consistent with reduced Lewis basicity of the ligand. The same trend is observed, for each ligand, when going from SnF_4 to $SnCl_4$ complexes, in agreement with the stronger Lewis acidity of SnF_4 which gives more stable complexes and higher *trans* ratios when compared to corresponding $SnCl_4$ complexes. This could also explain the fact that while the weakest ligands $R_2NP(O)F_2$ and $(CF_3CH_2)_3PO$ only form a *cis* isomer with $SnCl_4$, both *cis* and *trans* adducts are obtained with SnF_4 (see Table 2). Our solution NMR data suggest therefore that the weaker the Lewis basicity of the ligand and/or the acidity of the metal the more it forms higher *cis* ratios and the more the complex is labile, indicating a decrease in (the Lewis basicity of the ligand) complex stability in the

Table 2

Comparison of the approximate ${\it cis}$ isomer ratios in the complexes $[{\rm SnX_4L_2}]$ in dichloromethane.

Ligand (L)	% cis ^a		
	SnCl ₄	SnF ₄	
$(Me_2N)_3P(O)$	50 ^b	25 ^b	
$(Me_2N)_2P(O)F$	80 ^c	45 ^b	
$Me_2NP(O)F_2$	100 ^d	85 ^c	
(Me ₂ N) ₂ P(O)OCH ₂ CF ₃	40 ^b	32 ^b	
$Me_2NP(O)(OCH_2CF_3)_2$	65 ^b	42 ^b	
$P(O)(OCH_2CF_3)_3$	100 ^e	55 ^e	

^a Measured at slow exchange (b: at 298 K; c: 258 K; d: 198 K; e: 218 K) from 119 Sn (for SnCl₄) and 19 F (for SnF₄) NMR signals.

 $\begin{array}{ll} \mbox{order:} & (Me_2N)_3P(O) > (Me_2N)_2P(O)OCH_2CF_3 > Me_2NP(O)(OCH_2CF_3)_2 > (Me_2N)_2P(O)F > P(O)(OCH_2CF_3)_3 > Me_2NP(O)F_2. \end{array}$

3. Conclusions

New fluoroalkyl phosphoryl complexes with SnF_4 have been described and studied in solution by NMR spectroscopy. Our results show higher formation rates of the *trans* isomers in these complexes when compared to their corresponding $SnCl_4$ analogues. The latter were found to be more labile in solution than the former complexes. It has also been shown that while the weakest ligand, $(CF_3CH_2O)_3PO$, forms only a *cis* adduct with $SnCl_4$ both isomers are formed between this ligand and SnF_4 , presumably due to the greater Lewis acidity of the SnF_4 compared to $SnCl_4$. The lability of complex **5** compared to **1–4** is likely due to the lack of electron donating ability of dialkylamino groups and the presence of more electron withdrawing character of fluoroalkoxy groups in the ligand $(CF_3CH_2O)_3PO$.

4. Experimental

All preparations were carried out under a nitrogen atmosphere in solvents dried by standard techniques [24] and stored over molecular sieves. SnF₂ was obtained from Aldrich and used as received. The ligands $(R_2N)_2P(O)OCH_2CF_3$ [25], $R_2NP(O)(OCH_2CF_3)_2$ [25] and $P(O)(OCH_2CF_3)_3$ [26] were prepared as described in the literature. NMR spectra were recorded on a Bruker AV-300 instrument in CD₂Cl₂ as solvent; ³¹P at 121 MHz (85% H₃PO₄), ¹⁹F at 282 MHz (CFCl₃) and ¹¹⁹Sn at 111.8 MHz (SnCl₄). IR spectra were recorded on a Perkin Elmer Paragon 1000 PC spectrometer.

4.1. SnF₄[(R₂N)₂P(O)OCH₂CF₃]₂

A solution of $(R_2N)_2P(O)OCH_2CF_3$ (2.1 mmol) in CH₂Cl₂ (5 mL) was added to a suspension of SnF₄(MeCN)₂ (0.28 g, 1.0 mmol) in CH₂Cl₂ (20 mL) and the mixture stirred at room temperature for 2 h. The white precipitate was filtered off and dried in vacuo. (Yields R = Me (1): 0.47 g, 72% R = Et (2): 0.59 g, 77%.) *Anal.* Calcd. for C₁₄H₃₄F₁₀N₄O₄P₂Sn (1): C, 21.74; H, 4.26; N, 8.45. Found: C, 21.50; H, 4.33; N, 8.24. *Anal.* Calcd. for C₂₂H₅₀F₁₀N₄O₄P₂Sn (2): C, 30.99; H, 5.72; N, 7.23. Found: C, 30.85; H, 5.68; N, 6.89. IR (KBr): $\nu_{P=O}$ (1: 1208 cm⁻¹, 2: 1205 cm⁻¹); ν_{Sn-F} (1: 579 cm⁻¹, 2: 577 cm⁻¹).

4.2. $SnF_4[R_2NP(O)(OCH_2CF_3)_2]_2$

These compounds have been prepared similarly on mixing $SnF_4(MeCN)_2$ (0.28 g, 1.0 mmol) with $R_2NP(O)(OCH_2CF_3)_2$ (2.1 mmol) and stirring for 8 h. (Yields R = Me (**3**): 0.47 g, 61% R = Et (**4**): 0.58 g, 70%.) *Anal.* Calcd. for $C_{14}H_{26}F_{16}N_2O_6P_2Sn$ (**3**): C, 18.65; H, 2.61; N, 3.62. Found: C, 18.10; H, 2.84; N, 3.12. *Anal.* Calcd. for $C_{18}H_{34}F_{16}N_2O_6P_2Sn$ (**4**): C, 23.18; H, 3.40; N, 3.38. Found: C,

22.85; H, 3.29; N, 3.22. IR (KBr): IR (KBr): $v_{P=0}$ (**3**: 1245 cm⁻¹, **4**: 1242 cm⁻¹); v_{Sn-F} (570–585 cm⁻¹).

4.3. SnF₄[P(O)(OCH₂CF₃)₃]₂

This compound has been prepared similarly from SnF₄(MeCN)₂ (0.28 g, 1.0 mmol) and P(O)(OCH₂CF₃)₃ (2.1 mmol) and stirred for 24 h. Yield 0.47 g, 54%. *Anal.* Calcd. for C₁₄H₁₈F₂₂O₈P₂Sn (**5**): C, 16.33; H, 1.37. Found: C, 15.81; H, 1.15. IR (KBr): $\nu_{P=O}$ (1256 cm⁻¹); ν_{Sn-F} (586 cm⁻¹).

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