Journal of Fluorine Chemistry 132 (2011) 865–869

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Synthesis, characterization and solution behaviour of phosphoryl complexes of tin tetrafluoride

Med Abderrahmane Sanhoury [*], Med Taieb Ben Dhia, Med Rachid Khaddar

Laboratory of Coordination Chemistry, Department of Chemistry, Faculty of Sciences of Tunis, University of Tunis El Manar, 2092 Tunis, Tunisia

ARTICLE INFO

Article history:
Received 27 April 2011
Received in revised form 31 May 2011
Accepted 2 June 2011
Available online 13 June 2011

Keywords:
Phosphoryl ligands
Tin tetrafluoride
^{19}F NMR
^{119}Sn NMR
^{31}P NMR
Ligand exchange

ABSTRACT

The preparation and characterization of a series of octahedral complexes [SnF_4L_2] (L = $(Me_2N)_3PO$ (**1**), L = $(R_2N)_2P(O)F$; R = Me (**2**); Et (**3**) or L = $R_2NP(O)F_2$; R = Me (**4**); Et (**5**)) are described. These new adducts have been characterised by multinuclear (^{19}F, ^{31}P and ^{119}Sn) NMR, IR spectroscopy and elemental analysis. The NMR data particularly the ^{19}F NMR spectra showed that the complexes exist in solution as mixtures of *cis* and *trans* isomers. The solution behaviour of the complexes studied by variable temperature NMR in the presence of excess ligand indicated that, unlike in the $SnCl_4$ analogues, the ligand exchange at room temperature is slow for **1**–**3** and fast only for **4** and **5**. The metal–ligand exchange barriers in [SnF_4L_2] and [$SnCl_4L_2$] systems were estimated and compared. The results indicate that in addition to the difference in the Lewis acidity between SnF_4 and $SnCl_4$ the nature of the substituents (fluorine atoms) on the phosphorus atom of the ligand can contribute considerably to the lability of the complex obtained.

1. Introduction

Studies of tin(IV) complexes continue to provide fundamental information about both the Lewis acid–base model and the reactivity of tin(IV) species [1–4]. Tin(IV) chloride and bromide probably have the most extensive coordination chemistry and form octahedral complexes with phosphoryl ligands having the general formula [SnX_4L_2] (X = halide and L is the phosphoryl ligand) [5–9]. In these compounds two isomers, with the ligand L in *cis* or *trans* mutual orientations, are possible. Steric factors and the strength of both the Lewis basicity (i.e. the donor character of the P=O group of the ligand) and acidity (accepting ability of the metal centre) as well as other factors (solvent polarity, temperature, etc.) may be held responsible for the differences observed [5,10,11]. Although it was reported that Lewis acidity of the four tin(IV) halides is greatest for SnF_4 [12], the coordination chemistry of the latter is much less studied compared to the other SnX_4 (X = Cl, Br or I) units [12–14].

In a previous work, we have reported the synthesis and multinuclear NMR characterization of $SnCl_4$ complexes with the ligands $(R_2N)_2P(O)F$ [15] and $R_2NP(O)F_2$ [16] and showed that the predominant species was the *cis* isomer. This work is now being extended to the investigation of the SnF_4 adducts and we report here the synthesis and spectroscopic characterization of new SnF_4 complexes with $R_2NP(O)F_2$, $(R_2N)_2P(O)F$ and $(Me_2N)_3PO$. In contrast to $SnCl_4$ analogues [15,16], the results obtained for these SnF_4 complexes show that, on the basis of ^{19}F NMR spectra, their *trans* and *cis* isomers could be nicely assigned even at room temperature.

2. Results and discussion

2.1. Synthesis

Since anhydrous SnF_4 has a polymeric sheet structure [17], it is unreactive towards neutral ligands. A convenient method for the synthesis of its complexes is provided by $SnF_4(MeCN)_2$ made from SnF_2, I_2 and MeCN as described by Tudela and co-workers [18,19]. Treatment of $SnF_4(MeCN)_2$ in anhydrous dichloromethane solution with $R_2NP(O)F_2$, $(R_2N)_2P(O)F$ (R = Me or Et) or $(Me_2N)_3P(O)$ gives white solids with the composition [SnF_4L_2] (L = phosphoryl ligand). The solids are soluble in dichloromethane and chloroform with $R_2NP(O)F_2$ adducts being moderately soluble. The complexes could be recrystallised from a large volume of anhydrous dichloromethane. They were characterised by elemental analysis and particularly by their NMR data and comparison with the corresponding data for the free ligands.

2.2. Spectroscopic studies

The infrared spectra show strong bands within the range 1123 for **1**, 1260–1270 for **2** and **3** and 1290–1320 cm^{-1} for **4** and **5** attributed to $\nu_{P=O}$. The P=O stretching vibration is shifted towards

---

[*] Corresponding author. Tel.: +216 98269495; fax: +216 71885008.
E-mail address: senhourry@yahoo.com (M.A. Sanhoury).

0022-1139/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2011.06.001

Table 1
NMR data (δ/ppm and J/Hz) for the complexes [SnF_4L_2] in CD_2Cl_2.

Ligand (L)		^{31}P	^{19}F	^{119}Sn	$^1J_{P-F}$	$^1J_{Sn-F}$	$^2J_{Sn-P}$	$^2J_{F-F}$	$^3J_{P-F}$
$(Me_2N)_3P(O)$	*cis*	25.6	−151(t,t), −159(t)	−656	–	1838	–	50.8	5.65
	trans	25.8	−153(t)	−659	–	1660	28.53	–	4.23
$(Me_2N)_2P(O)F$	*cis*	17.6	−83.5(d), −152(t,t), −165(t)	−651	944	1926	–	53.65	5.65
	trans	18.0	−83.3(d), −154(t)	−653	945	1734	26.31	–	2.82
$(Et_2N)_2P(O)F$	*cis*	15.2	−78.6(d), −151(t), −163(t)	−656	966	1931	–	53.66	–
	trans	15.4	−78.4(d), −153(t)	−659	966	1731	26.42	–	–
$Me_2NP(O)F_2$[a]	*cis*	−6.54	−81.5(d), −153(t), −170(t)	−651	1011	2061	–	59.30	–
	trans	−6.29	−81.1(d), −156(s)	−656	1017	1827	–	–	–
$Et_2NP(O)F_2$[b]	*cis*	−5.27	−78.5(d), −152(t), −169(t)	−652	1018	2053	–	59.30	–
	trans	−4.98	−78.4(d), −155(s)	−657	1022	1824	–	–	–

[a] At 248 K.
[b] At 268 K.

lower wave numbers on coordination to the tin atom compared with its value for the free ligands. The coordination shift is consistent with phosphoryl coordination to the tin atom. This shift is 20 cm^{-1} for $Me_2NP(O)F_2$ against 85 cm^{-1} for HMPA [5] explaining the difference in the basicity strength between these two ligands which is most probably due to the substitution of two dimethylamino groups by two fluorine atoms. The absorption band at 560–590 cm^{-1} corresponds to a stretching vibration of the Sn–F group.

The NMR data show the presence of both *cis* and *trans* isomers in dichloromethane solution for all the complexes prepared (Table 1). The approximate isomer ratio was determined from the $^{19}F\{^1H\}$ NMR spectra. For complexes **2** and **3** the two isomers have similar abundance but while the *trans* isomer predominates for complex **1**, the *cis* form is the major isomer in complexes **4** and **5**. Despite the fact that resonances were observed at ambient temperatures in the ^{31}P, ^{19}F and ^{119}Sn NMR spectra of complexes **1**–**3**, the corresponding spectra of complexes **4** and **5** showed broad and poorly resolved features and the solutions were cooled to 258 K to improve resolution.

The ^{31}P NMR spectra show resonances (singlet for **1**, doublet for **2** and **3** and triplet for **4** and **5**) for each isomer with very similar chemical shifts and weak $^{117/119}Sn$ satellites. The ^{19}F NMR spectra are more useful and show, in the SnF_4 region, singlet resonances for the *trans* isomers and two triplets for the *cis* with clearly resolved $^1J(^{119}Sn{-}^{19}F)$ and $^1J(^{117}Sn{-}^{19}F)$ (Fig. 1). For complexes **2**–**5**, the ^{19}F spectra (Fig. 2) also show, in the region of the ligand fluorine atoms, two doublets for the *cis* and *trans* isomers with ^1J(P–F) as indicated in Table 1.

The ^{119}Sn NMR spectra show also the presence of both *cis* and *trans* isomers. This was observed at ambient temperatures for **1**–**3** as a symmetrical quintet of triplets for the *trans* isomer and a multiplet (t,t,t) for the *cis* isomer (Fig. 3) with coupling constants consistent with those obtained from the $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ spectra. These data are in good agreement with those obtained for related complexes [12]. For complexes **4** and **5**, the ^{119}Sn resonances are broad and ill-defined at ambient temperatures but on cooling the samples, the resonances sharpen and split and at 258 K give well defined features with predominance of the multiplet related to the *cis* isomer.

It is worth to note that, unlike the $SnCl_4$ analogues [15,16], complexes **2**–**5** show little or no dissociation in CH_2Cl_2 even with the weakest ligands, $R_2NP(O)F_2$. This is consistent with the stronger Lewis acidity of SnF_4, leading to higher *trans* ratios being formed with SnF_4 as compared to $SnCl_4$ complexes (Table 2). Comparison of these ratios with those obtained for [$SnF_4(Me_3PO)_2$] and [$SnF_4(Ph_3PO)_2$] [12] suggests that the donor power of the ligand Me_3PO is very similar to that of $(Me_2N)_3PO$, while the ligands Ph_3PO and $(Me_2N)_2P(O)F$ form similar *cis*:*trans* ratios showing nearly identical donor power. Both [$SnF_4(Me_3PO)_2$] and

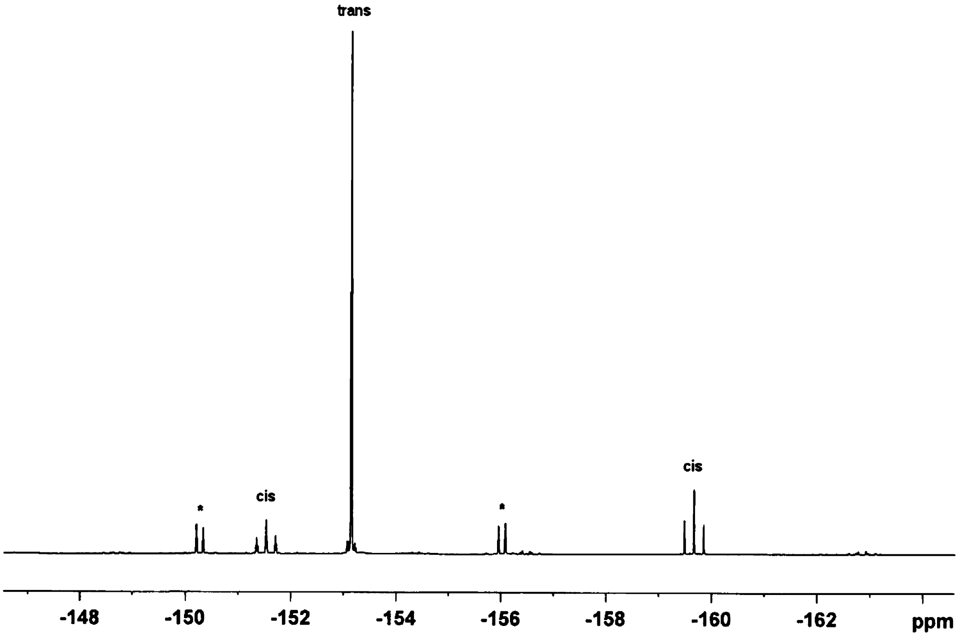

Fig. 1. $^{19}F\{^1H\}$ NMR spectrum of **1** in CD_2Cl_2 at 298 K (* indicates $^{119/117}Sn$ satellites in the *trans* isomer).

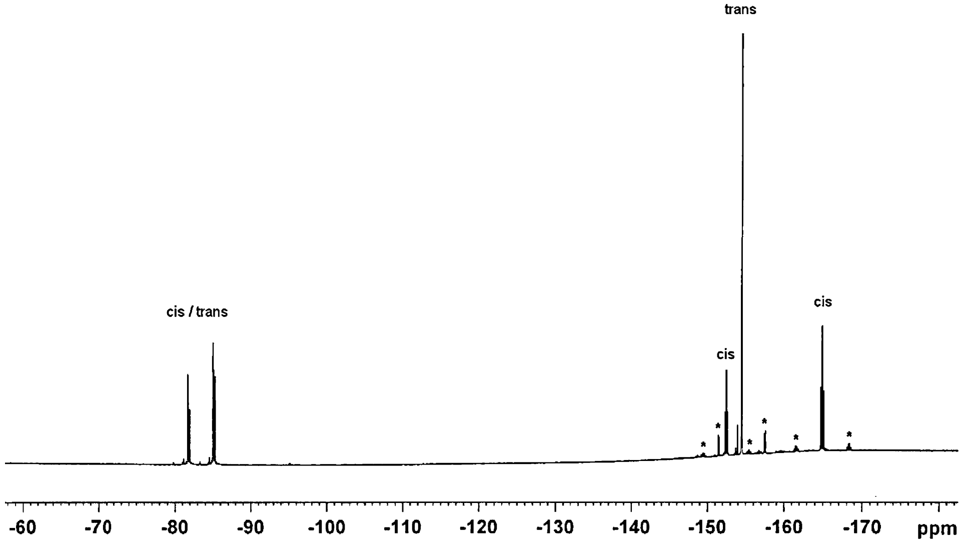

Fig. 2. $^{19}F\{^1H\}$ NMR spectrum of **2** in CD_2Cl_2 at 298 K (* indicates $^{119/117}Sn$ satellites).

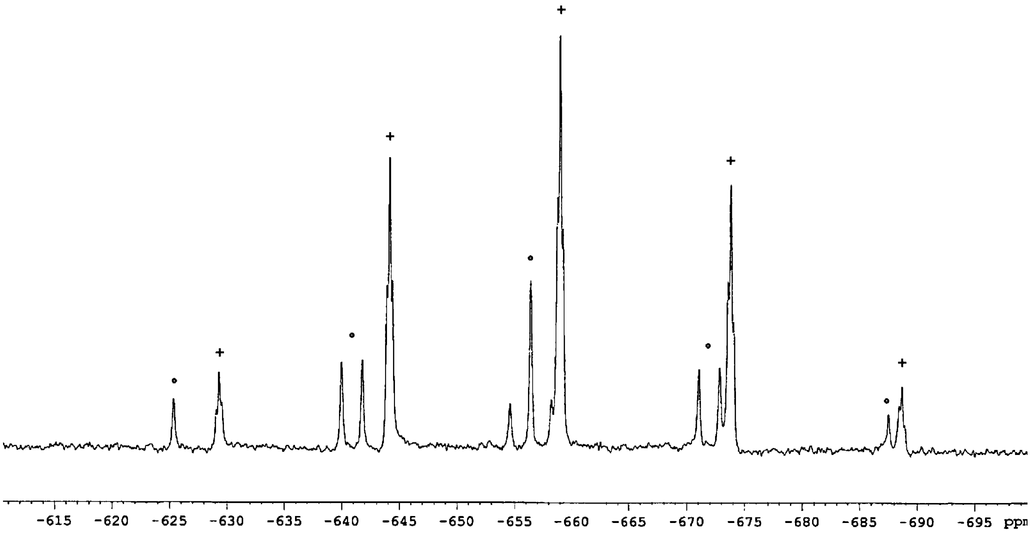

Fig. 3. ^{119}Sn NMR spectrum of **1** in CD_2Cl_2 at 298 K (°: *cis* and +: *trans* multiplets).

$[SnF_4(Me_2N)_3PO)_2]$ solids show also very similar Sn–F stretching vibrations. This would indicate that the structure of the latter complex is *trans* in solid state as is the case of $[SnF_4(Me_3PO)_2]$ [12].

In order to study the solution behaviour of the complexes prepared and compare them to their $SnCl_4$ analogues, excess ligand was added to CH_2Cl_2 solutions of **1**–**5**. The ^{31}P and ^{19}F NMR spectra of these solutions display for complexes **1**–**3** separate signals for free, *cis* and *trans* ligands, showing that no ligand exchange is occurring at room temperature in these complexes (Fig. 4). However, the solution spectra of **4** and **5** show at room

Table 2
Approximate *cis* isomer ratios in the complexes $[SnX_4L_2]$ in dichloromethane and their metal–ligand exchange barriers (ΔG^*/kcal mol^{-1}).

Ligand (L)	% *cis*[a]		ΔG^{*e}	
	$SnCl_4$	SnF_4	$SnCl_4$	SnF_4
$(Me_2N)_3P(O)$	50[b]	25[b]	16.87[f]	>18.10
$(Me_2N)_2P(O)F$	80[c]	45[b]	13.80	16.30
$Me_2NP(O)F_2$	100[d]	85[c]	9.75	13.50

a: measured at slow exchange (b: at 298; c: 258; d: 198 K) from ^{119}Sn (for $SnCl_4$) and ^{19}F (for SnF_4) NMR signals, e: calculated from Eyring equation at T_c using ^{19}F NMR spectroscopy and f: value taken from Ref. [23].

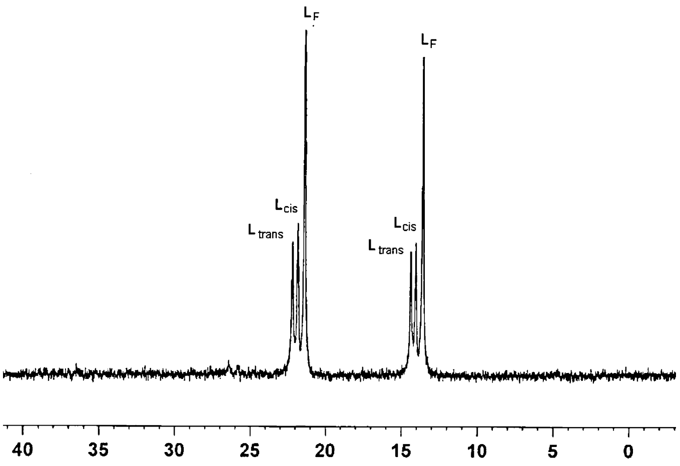

Fig. 4. $^{31}P\{^1H\}$ NMR spectrum of **2** in the presence of excess ligand in CD_2Cl_2 at 298 K (L_F, L_{cis} and L_{trans} indicate the ligand in the free, *cis* and *trans* positions, respectively).

temperature average signals which broaden and split on cooling and give at 258 K separate signals for free, *cis* and *trans* ligands. This indicates that ligand exchange at room temperature is slow on the NMR time scale for **1**–**3** and fast for complexes **4** and **5**.

For comparison purposes, the coalescence temperatures for ligand exchange were estimated for the three complexes **1**, **2**, **4**, and their $SnCl_4$ analogues and the exchange barriers have been determined from the ^{19}F NMR data using the Eyring equation (1) together with Eq. (2) [20]:

$$k_c = \left(\frac{kT}{h}\right) \exp\left(-\frac{\Delta G}{RT}\right) \tag{1}$$

$$\Delta G^{\neq} = 19.14\, T_c \left(10.32 + \log\left(\frac{T_c}{k_c}\right)\right) \times 10^{-3} \tag{2}$$

where k_c is the exchange rate $((\pi \times \Delta\upsilon)/2^{1/2})$ at T_c and $\Delta\upsilon$ the peak separation in the absence of exchange. The calculated metal–ligand exchange barriers are gathered in Table 2.

The coalescence temperatures (T_c) were found to be unaffected by added ligand, which together with our previous results on other related $SnCl_4$ complexes [21] may indicate that the ligand exchange mechanism is dissociative proceeding via a five-coordinate intermediate, in agreement with trends generally observed for tin tetrahalide adducts [22].

Examination of Table 2 shows, for each tin halide, that the decrease in the metal–ligand exchange barriers is accompanied by higher *cis* ratios and a decrease of the complex stability as expected, in the order: $(Me_2N)_3P(O) > (Me_2N)_2P(O)F > Me_2NP(O)F_2$, consistent with reduced Lewis basicity of the ligand as the substituents on the phosphorus atom become more electronegative. The same trend is observed, for each ligand, when passing from SnF_4 to $SnCl_4$ complexes. In this case and since the ligand is kept constant, a decrease in the exchange barrier of 2.5 kcal mol^{-1} for $(Me_2N)_2P(O)F$ may indicate the difference in the strength of the bonding interaction with this ligand between SnF_4 and $SnCl_4$, in good agreement with the stronger Lewis acidity of SnF_4 (see Table 2). Our solution NMR data suggest that the weaker the Lewis basicity of the ligand the more it forms higher *cis* ratios and the more the complex is labile, and vice versa.

3. Conclusions

A series of new phosphoryl complexes with SnF_4 have been synthesised and studied in solution by NMR spectroscopy. It was shown that the rates of formation of the *trans* isomer in these complexes are higher than those formed in their $SnCl_4$ analogues. Even with the weakest ligand, $R_2NP(O)F_2$, the *trans* isomer was found to be formed together with the *cis* isomer. Interestingly, our variable temperature NMR studies indicate that, in the presence of excess ligand, the metal–ligand exchange is slower on the NMR time scale for SnF_4 than for $SnCl_4$. This further supports the greater Lewis acidity of the SnF_4. The difference in the strength of the Sn–L interactions could be important for the catalytic activity of these complexes. Preparation of related tin compounds with various lability of Sn–L coordination for use as active catalysts is under way in our laboratory.

4. Experimental

All preparations were carried out under a nitrogen atmosphere in solvents dried by standard techniques [24] and stored over molecular sieves. SnF_2 was obtained from Aldrich and used as received. Hexamethylphosphoramide, $(Me_2N)_3PO$ (Fluka), was purified by distillation before use. The ligands $(R_2N)_2P(O)F$ [25,26] and $R_2NP(O)F_2$ [27,28] were prepared according to methods described in literature, while the complexes were prepared in a similar manor to the method reported by Davis et al. [12]. NMR spectra were recorded on a Bruker AV-300 instrument in CD_2Cl_2 as solvent; ^{31}P at 121 MHz (85% H_3PO_4), ^{19}F at 282 MHz ($CFCl_3$) and ^{119}Sn at 111.8 MHz ($SnCl_4$). IR spectra were recorded on a Perkin Elmer Paragon 1000 PC spectrometer.

4.1. *[SnF₄((Me₂N)₃PO)₂]*

A solution of $(Me_2N)_3PO$ (0.37 g, 2.1 mmol) in CH_2Cl_2 (5 mL) was added to a suspension of $SnF_4(MeCN)_2$ (0.28 g, 1.0 mmol) in CH_2Cl_2 (20 mL) and the mixture stirred at room temperature for 2 h. The white precipitate was filtered off and dried *in vacuo*. Yield: 0.46 g, 84%. *Anal.* Calcd. for $C_{12}H_{36}F_4N_6O_2P_2Sn$ (**1**): C, 26.06; H, 6.56; N, 15.19. Found: C, 25.88; H, 6.60; N, 15.31. IR (KBr): $\nu_{\text{P=O}}$ (1123 cm^{-1}); $\nu_{\text{Sn–F}}$ (576 cm^{-1}).

4.2. *[SnF₄((R₂N)₂P(O)F)₂]*

Prepared similarly from $SnF_4(MeCN)_2$ (0.28 g, 1.0 mmol) and $(R_2N)_2P(O)F$ (2.1 mmol) and stirred for 6 h (Yields R = Me (**2**): 0.40 g, 78% R = Et (**3**): 0.49 g, 80%). *Anal.* Calcd. for $C_8H_{24}F_6N_4O_2P_2Sn$ (**2**): C, 19.10; H, 4.81; N, 11.14. Found: C, 19.31; H, 4.93; N, 11.45. *Anal.* Calcd. for $C_{16}H_{40}F_6N_4O_2P_2Sn$ (**3**): C, 31.24; H, 6.55; N, 9.11. Found: C, 31.70; H, 6.61; N, 8.96. IR (KBr): $\nu_{\text{P=O}}$ (1260–1270 cm^{-1}); $\nu_{\text{Sn–F}}$ (570–585 cm^{-1}).

4.3. *[SnF₄(R₂NP(O)F₂)₂]*

Prepared similarly from $SnF_4(MeCN)_2$ (0.28 g, 1.0 mmol) and $R_2NP(O)F_2$ (2.1 mmol) and stirred for 8 h (Yields R = Me (**4**): 0.28 g, 63%, R = Et (**5**): 0.31 g, 62%). *Anal.* Calcd. for $C_4H_{12}F_8N_2O_2P_2Sn$ (**4**): C, 10.61; H, 2.67; N, 6.19. Found: C, 10.17; H, 2.64; N, 6.05. *Anal.* Calcd. for $C_8H_{20}F_8N_2O_2P_2Sn$ (**5**): C, 18.88; H, 3.96; N, 5.50. Found: C, 18.21; H, 3.91; N, 5.45. IR (KBr): $\nu_{\text{P=O}}$ (1290–1320 cm^{-1}); $\nu_{\text{Sn–F}}$ (580–600 cm^{-1}).

Acknowledgements

We are grateful to the Tunisian Ministry of High Education and Scientific Research for financial support (LR99ES14) of this research and to Professor Emeritus A. Baklouti of the Department of Chemistry, Faculty of Sciences of Tunis, University of Tunis El Manar for his valuable help and continuous support.

References

[1] D. Fàrsaiu, R. Leu, P.J. Ream, J. Chem. Soc. Perkin Trans. 2 (2001) 427–431.
[2] S.E. Dann, A.R.J. Genge, W. Levason, G. Reid, J. Chem. Soc. Dalton Trans. (1997) 2207–2213.
[3] C.H. Yoder, L.A. Margolis, J.M. Horne, J. Organomet. Chem. 633 (2001) 33–38, and references therein.
[4] H.R. Hays, D.J. Peterson, in: G.M. Kosolopoff, L. Mair (Eds.), Organic Phosphorus Compounds, vol. 3, Wiley, New York, 1972.
[5] E. Le Coz, J.E. Guerchais, Bull. Soc. Chim. Fr. (1971) 80–87.
[6] S.J. Ruzicka, A.E. Merbach, Inorg. Chim. Acta 20 (1976) 221–229.
[7] L.A. Aslanov, V.M. Ionov, V.M. Attiya, A.B. Permin, V.S. Petrosyan, Zh. Strukt. Khim. 18 (1977) 1103–1112.
[8] S.J. Ruzicka, A.E. Merbach, Inorg. Chim. Acta 22 (1977) 191–200.
[9] S.E. Denmark, X. Su, Tetrahedron 55 (1999) 8727–8738.
[10] D. Tudela, V. Fernàndez, J.D. Tornero, J. Chem. Soc. Dalton Trans. (1985) 1281–1284.
[11] J. Rupp-Bensadon, E.A.C. Lucken, J. Chem. Soc. Dalton Trans. (1983) 495–497.
[12] M.F. Davis, W. Levason, G. Reid, M. Webster, Polyhedron 25 (2006) 930–936, and references therein.
[13] M.F. Davis, M. Clarke, W. Levason, G. Reid, M. Webster, Eur. J. Inorg. Chem. (2006) 2773–2782.
[14] M.F. Davis, W. Levason, G. Reid, M. Webster, W. Zhang, Dalton Trans. (2008) 533–538.

[15] M.A.M. Khouna, M.T. Ben Dhia, M.R. Khaddar, Phosphorus Sulfur Silicon 180 (2005) 1673–1682.
[16] M.A.M. Khouna Sanhoury, M.T. Ben Dhia, K. Essalah, M.R. Khaddar, Polyhedron 25 (2006) 3299–3304.
[17] M. Bork, R. Hoppe, Z. Anorg. Allg. Chem. 622 (1996) 1557–1563.
[18] D. Tudela, F. Rey, Z. Anorg. Allg. Chem. 575 (1989) 202–208.
[19] D. Tudela, J.A. Patron, Inorg. Synth. 31 (1997) 92–93.
[20] H. Friebolin, Basic One- and Two-Dimensional NMR Spectroscopy, Wiley-VCH, Weinheim, Germany, 1991, p. 263.
[21] M.A.K. Sanhoury, M.T. Ben Dhia, M.R. Khaddar, Inorg. Chim. Acta 362 (2009) 3763–3768.
[22] L. Helm, A.E. Merbach, Chem. Rev. 105 (2005) 1923–1959, and references therein.
[23] S.J. Ruzicka, C.M.P. Favez, A.E. Merbach, Inorg. Chim. Acta 23 (1977) 239–247.
[24] W.L.F. Armarego, D.D. Perrin, Purification of Laboratory Chemicals, 14th ed., Butterworth-Heinemann, Oxford, 1996.
[25] E.A. Robinson, D.S. Lavery, Spectrochim. Acta 28A (1972) 1099, and references therein.
[26] G. Schrader, Monographie N◦. 62 zu “Angewandte Chemie” und “Chemie—Ingenieur—Technik”, Verlag Chemie, Weinheim/Bergstrasse, 1951.
[27] G. Schrader, B.I.O.S. Report No. 1103, London, 1945.
[28] A. Kovache, H. Jean, G. Garnier, Chim. Ind. 64 (1950) 287.