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The reaction of 2-formylpyridine thiosemicarbazone (HFPT) with tin tetrahalides. Crystal and molecular structure of [$SnCl_3$(FPT)]

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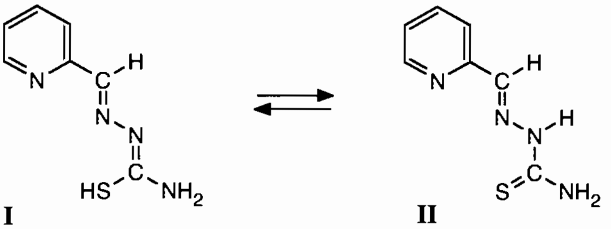
Abstract

2-Formylpyridine thiosemicarbazone (HFPT) reacts with the tin tetrahalides (X = Cl, Br, I) with abstraction of HX and the formation of tridentate N,N,S-bonded hexacoordinated species [SnX_3(FPT)]. A single crystal X-ray diffraction study of the chloro complex establishes *mer*-isomerism. Mössbauer data of the products correlate very well with a rehybridization of tin from sp^3 to d^2sp^3 upon complexation.

Introduction

There has been considerable interest in recent years in transition metal complexes of 2-formylpyridine thiosemicarbazone (HFPT) due to their notable biological activity as antitumor agents [1, 2]. Tin chemistry also presents many examples of biological action [3]; moreover, since tin displays a very interesting chemistry of its own, it was deemed worthwhile to investigate the mode of interaction of the tin tetrahalides, SnX_4 (X = Cl, Br, I), towards 2-formylpyridine thiosemicarbazone.

The ligand presents two tautomers designated by I and II. It can originate tridentate complexes either in its protonated or deprotonated forms [1, 4].



I

II

Experimental

HFPT was prepared according to standard procedures [5].

The complexes were obtained by the addition of a slight excess of SnX_4 to an EtOH solution of HFPT near its boiling point. A precipitate was readily formed; this was filtered, washed with ether and recrystallized from a 1:1 mixture of MeOH and EtOH. The products were insoluble in other solvents. They were dried under vacuum over $CaCl_2$. The chloro and bromo complexes were yellow, and the iodo complex was orange. A similar reaction performed with Me_3SnCl led to no result.

C, H, N analyses gave the following results:

1. Found: C, 20.8; H, 1.6; N, 12.6. Calc. for $SnCl_3C_7H_7N_4S$: C, 20.8; H, 1.8; N, 13.9%.

2. Found: C, 16.0; H, 1.1; N, 10.3. Calc. for $SnBr_3C_7H_7N_4S$: C, 15.6; H, 1.3; N, 10.4%.

3. Found: C, 13.9; H, 1.0; N, 8.9. Calc. for $SnI_3C_7H_7N_4S$: C, 12.4; H, 1.0; N, 8.3%.

All three complexes decompose upon heating: **1** at 250 °C, **2** at 275 °C, **3** at 227 °C.

IR spectra were run in a Perkin-Elmer 283 B instrument using CsI pellets.

Mössbauer spectra were obtained from a constant acceleration spectrometer moving a $CaSnO_3$ source at room temperature. The samples were analysed at 85 K. All spectra were computer-fitted assuming Lorentzian single lines.

The ^{119}Sn NMR spectrum of a MeOH solution of the chloro complex was recorded in a 300 MHz Bruker spectrophotometer. Poor solubility restricted the use of NMR to this complex only.

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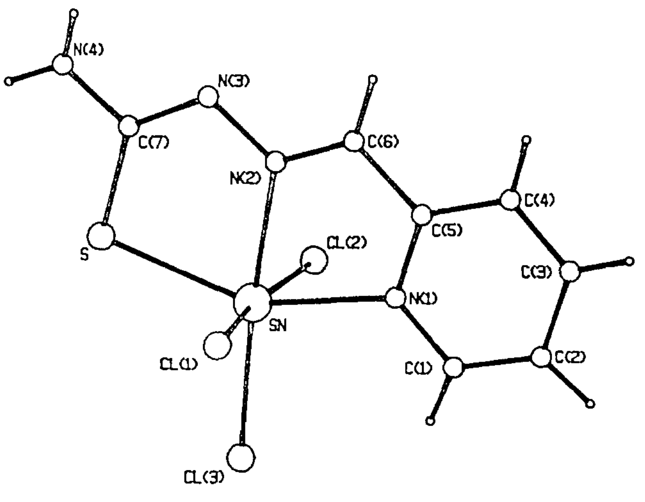

Fig. 1. Molecular structure of [$SnCl_3$(FPT)].

The molecular structure of the chloro complex, obtained from a single crystal X-ray diffraction study, is shown in Fig. 1.

Crystal data: $C_3H_7Cl_3N_4SSn$, $M=404.3$, monoclinic space group $P2_1/n$, $a=7.223(1)$, $b=13.370(3)$, $c=13.969(2)$ A; $\alpha=90$, $\beta=99.27$, $\gamma=90°$, $U=1331.5$ A^3, $Z=4$, $D_{calc}=2.02$ g cm^{-3}. Monochromated Mo Kα radiation $\lambda=0.71069$ A, $\mu=26.6$ cm^{-1}. The structure of the crystal ($0.3\times0.2\times0.1$ mm) was solved by routine heavy atom techniques and refined by full matrix least-squares methods, using an Enraf-Nonius CAD-4 diffractometer, with non-H atoms isotropic. Of 2647 reflections observed, 2036 with $|F^2|>2\sigma(F^2)$ were used in the refinement, which converged at $R=0.022$, $R_w=0.032$.

Results and discussion

The products are formed with HX elimination and, as X-ray crystallographic structural data demonstrate that the chloro complex is the *mer*-isomer, it is likely that the others are also hexacoordinated with the same structure, the ligand acting as a tridentate species. The loss of HX, leading to the thiolate form of the ligand, is quite interesting if one compares the carbon tetrahalides with the corresponding tin tetrahalides. Whereas $SnCl_4$, as we have shown, can lose a chloride ion in the presence of HFPT and expand the coordination number of tin, no such thing can occur with CCl_4, which is reasonably inert. The availability of empty low-energy orbitals in tin as well as its metallic character makes $SnCl_4$ quite different from its congener CCl_4.

The ^{119}Sn NMR spectrum of [$SnCl_3$(FPT)] in MeOH showed a chemical shift of -481.5 ppm relative to Me_4Sn, which is considerably upfield compared with $SnCl_4$, for which $\delta=-150$ ppm [6]. This shift to higher field is consistent with the increase in the coordination number of tin from four to six and a corresponding greater shielding of the tin nucleus.

The ^{119}Sn Mössbauer spectrum of [$SnCl_3$(FPT)] is shown in Fig. 2. No quadrupole splitting is observed, and the same is true for the spectra of the other two complexes. Table 1 gives the Mössbauer experimental data, as well as those of the parent tin tetrahalides.

The absence of any quadrupole splitting in the Mössbauer spectra of the three complexes shows that they have a highly symmetrical electronic density distribution around the tin atom. This can be interpreted in terms of tin having six equivalent d^2sp^3 hybrid orbitals. These new hybrids replace the four sp^3 hybrids of the tetrahalides. It is well known that the isomer shift, δ, is directly proportional to the percent s character of tin in its compounds [8]. Thus replacement of a ligand by a more electronegative group or expansion of the coordination number of tin will lead to a decrease in the isomer shift. By plotting the Pauling electronegativities of Cl, Br and I against the isomer shifts of the tetrahalides an inverse linear correlation was obtained. An inverse linearity was also produced for the complexes, even though tin has now an expanded coordination. In the formation of our complexes the percent s character of tin changes from 25% (sp^3) to 16.67% (d^2sp^3), a relative

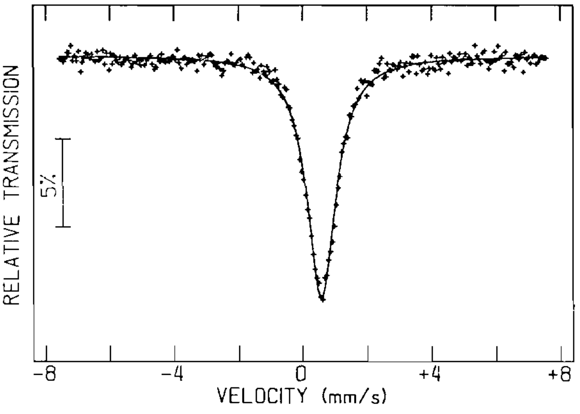

Fig. 2. ^{119}Sn Mössbauer spectrum of [$SnCl_3$(FPT)].

TABLE 1. Mössbauer parameters (relative to a $CaSnO_3$ source)

Compound	δ (mm s^{-1})	Δ (mm s^{-1})	Γ (mm s^{-1})
[$SnCl_3$(FPT)] (1)	0.585(6)	0	1.08(1)
[$SnBr_3$(FPT)] (2)	0.752(4)	0	0.96(1)
[SnI_3(FPT)] (3)	1.01(1)	0	1.09(1)
$SnCl_4$	0.82(1)[a]	0	
$SnBr_4$	1.13(1)[a]	0	
SnI_4	1.545(8)[a]	0	

[a] Ref. 7.

variation of 0.33. The data in Table 1 give actual relative variations of 0.29 for the chloro, 0.33 for the bromo and 0.35 for the iodo complex, respectively.

The IR spectra of the complexes present characteristic features, as compared to that of the free ligand. Table 2 shows the data for the Sn–ligand vibrations.

Several of the ν(CS) bands in FPT either disappear completely or are extremely reduced in intensity. On the other hand shifts in ν(CS) absorptions are likely, due to thiolate formation and Sn–S bonding in the complexes. A set of four intense bands at 1100, 1089, 1052 and 982 cm^{-1} in free HFPT becomes very feeble upon complexation. This set of bands is believed to have some CS stretching component [9]. Free HFPT also displays a strong well-defined band at 805 cm^{-1}, which is usually assigned to the νCS vibration with some contribution from either δNH_2 or νCN [9, 10]. This band disappears entirely in the spectra of the chloro and the bromo complexes, and appears as a very weak absorption in the iodo complex, with no variation in wavenumber. Another band assigned to $\nu CS + \nu CN$ appears at 723 cm^{-1} in the free ligand, and is shifted to 712, 710 and 705 cm^{-1} in the chloro, bromo and iodo complexes, respectively. Very similar results have been reported in the literature [11]. A new band is also present in the complexes, in the same order as above, at 571, 572 and 570 cm^{-1}. Although most authors describe a marked downward shift in the 805 cm^{-1} band of free HFPT, of over 100 cm^{-1}, as a result of a lower CS bond order in the complexes compared to the ligand [9, 10], the bands at *c.* 570 cm^{-1} seem to exhibit too great a shift to correspond to the 805 cm^{-1} band in the ligand. However, there is no other new absorption in this region of the spectrum.

The chloro complex is the only one to show an Sn–X absorption band, in the range under investigation (4000–200 cm^{-1}). This is quite characteristic and appears at 281 cm^{-1}, in accordance with many other examples [12]. The Sn–Br and Sn–I vibrations did not occur in the wavenumber range under study due to their greater reduced mass.

The Sn–N vibration (imine nitrogen) was assigned to the absorptions at 320 cm^{-1} for both the chloro and the bromo complexes, and at 309 cm^{-1} for the iodo complex. These assignments are quite consistent with literature data and with values obtained in our laboratory [12]. The Sn–N vibration (pyridine ring nitrogen), which tends to occur at high wavenumbers, was assigned to bands at 480, 472 and 452 cm^{-1} for the chloro, bromo and iodo complexes, respectively. Again this fitted quite well with literature data and with cases previously studied [11, 12]. The Sn–S vibration occurs near 350 cm^{-1}, in general a little above this value [11, 13]. The only unassigned band was that at 400 cm^{-1} for both the chloro and the bromo complexes, and at 392 cm^{-1} for the iodo complex. These absorptions were tentatively assigned to the Sn–S vibration.

TABLE 2. IR data for Sn–ligand vibrations (cm^{-1})

Compound	ν(Sn–S)	ν(Sn–N) pyridine ring nitrogen	ν(Sn–N) imine nitrogen	ν(Sn–X) X = halogen
[$SnCl_3$(FPT)] (**1**)	400	480	320	281
[$SnBr_3$(FPT)] (**2**)	400	472	320	
[SnI_3(FPT)] (**3**)	392	452	309	

Molecular structure of [$SnCl_3$(FPT)]

The molecular structure shown in Fig. 1 reveals the presence of a six-coordinate tin(IV) atom, which is ligated to three chlorine atoms, two nitrogen atoms and one sulfur atom of the FPT ligand. The roughly octahedral complex has the meridional configuration of the three chlorine atoms, with the two chlorines *trans* to each other exhibiting slightly longer bond lengths to tin than the chlorine which is *trans* to nitrogen(2). The molecular structure of the FPT ligand exerts some constraints on the idealized octahedral geometry around the Sn(IV) atom and, in particular, the SSnN(1) bond angle (153°) is much less than expected. The two SnN bond lengths are also significantly different, probably resulting from the geometrical features of the ligand. The distances N(2)–C(6) and N(3)–C(7) are 1.324(4) and 1.275(4) Å, respectively. The values are similar, although the former is longer than the latter. This similarity of values is consistent with the first tautomeric form. The difference in length between the two NC

TABLE 3. Selected interatomic distances (A) and angles (°)

Sn–Cl(1)	2.433(1)	Sn–Cl(2)	2.415(1)
Sn–Cl(3)	2.360(1)	Sn–S	2.463(1)
Sn–N(1)	2.225(3)	Sn–N(2)	2.194(2)
S–C(7)	1.753(3)	N(1)–C(1)	1.347(4)
N(1)–C(5)	1.344(4)	N(2)–N(3)	1.368(3)
N(2)–C(6)	1.275(4)	N(3)–C(7)	1.324(4)
C(5)–C(6)	1.460(4)		
Cl(1)–Sn–Cl(2)	170.01(4)	Cl(1)–Sn–Cl(3)	90.45(3)
Cl(1)–Sn–S	94.42(3)	Cl(1)–Sn–N(1)	83.77(7)
Cl(1)–Sn–N(2)	87.59(7)	Cl(2)–Sn–Cl(3)	91.08(3)
Cl(2)–Sn–S	94.65(4)	Cl(2)–Sn–N(1)	86.25(7)
Cl(2)–Sn–N(2)	89.96(7)	Cl(3)–Sn–S	105.92(3)
Cl(3)–Sn–N(1)	100.65(7)	Cl(3)–Sn–N(2)	174.41(7)
S–Sn–N(1)	153.39(7)	S–Sn–N(2)	79.46(7)
N(1)–Sn–N(2)	73.94(9)	Sn–S–C(7)	95.3(1)
Sn–N(1)–C(5)	114.0(2)	Sn–N(2)–N(3)	122.3(2)
Sn–N(2)–C(6)	117.6(2)	N(2)–N(3)–C(7)	114.3(2)
N(1)–C(5)–C(6)	117.0(3)	N(2)–C(6)–C(5)	117.4(3)
S–C(7)–N(3)	128.6(2)		

distances may be ascribed to some degree of delocalization along N(3)–C(7)–S.

It is thus clear from the structural study that the reaction product is derived from loss of HCl from the interaction of the SH group in the tautomeric form **I** of the FPT ligand with $SnCl_4$.

Table 3 gives the most important interatomic distances and angles.

Supplementary material

All other intramolecular distances and angles as well as atomic and thermal parameters are available from the authors on request.

Acknowledgements

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