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Coordinative Interactions Involving Dichlorodiphenyltin(IV) and Tin Tetrachloride with Polydentate N,O-Ligands

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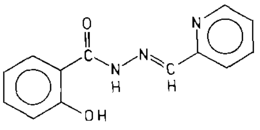
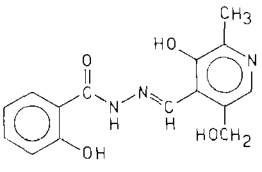
Twelve tin(IV) complexes obtained from the reaction of Ph_2SnCl_2 and $SnCl_4$ with six polydentate ligands containing $>C=O$ and $>C=N-$ groups have been examined by vibrational and electronic spectroscopy and conductivity measurements. On the basis of these studies, the ligand behaviour and the probable structure of the complexes were discussed.

Introduction

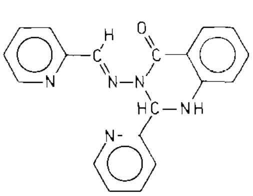
In previous papers we have investigated the chelating properties of the following polydentate ligands in some transition metal complexes[1–6]:



HSIP

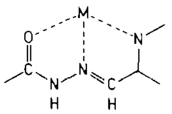


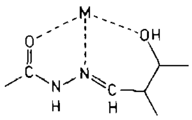
HSIPOX



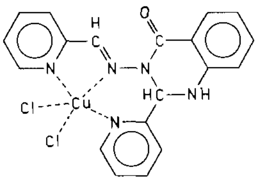
AIP

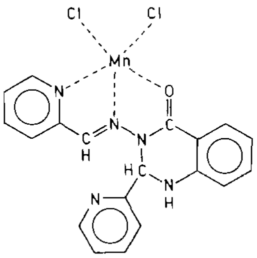
From X-ray and spectroscopic analyses it has been established that HSIP and HSIPOX always behave as chelating terdentate ligands through the systems:



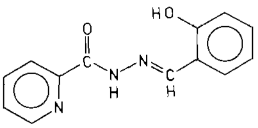


while for AIP, the X-ray analysis, carried out on Cu(AIP)Cl_2[4] and Mn(AIP)Cl_2[5] established the possibility of two different conformations in the ligand behaviour:

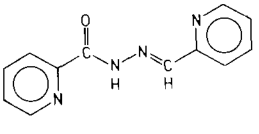




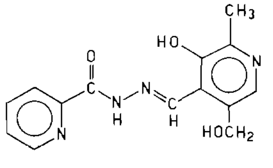
Continuing these studies we have now prepared some tin(IV) compounds from the reaction of dichlorodiphenyltin and tin tetrachloride with the above mentioned ligands and with the following other organic molecules:



HPIS



HPIP



HPIPOX

The probable structure of these new complexes is discussed in the present communication on the basis of the infrared and electronic spectra and molar conductance measurements.

Experimental

Synthesis of the Ligands

HSIP, HPIP, and AIP were prepared as previously described.[3,7,6]

HPIS, HSIPOX, and HPIPOX were synthesized by condensing salicylaldehyde with picolylhydrazide, pyridoxal with salicylhydrazide, and pyridoxal with picolylhydrazide respectively. The reactions were carried out in ethanol solution at reflux temperature for 1 hour. The melting points were: 220 (HSIP), 167 (HPIS), 161 (HPIP), 250 (HSIPOX), 248 (HPIPOX), 215° C (AIP).

Synthesis of the Tin Complexes

All the compounds were prepared by adding a solution of the ligand in a suitable solvent (see Table I) to a chloroform solution of dichlorodiphenyltin or to an ethanol solution of tin tetrachloride and allowing crystallization to occur. With $Sn(HPIP)Cl_4 \cdot H_2O$ the precipitation occurred on mixing. All the solvents were dried and purified before use.[8] Ph_2SnCl_2 was prepared as previously described.[9] The reactions were always carried out at room temperature in dry nitrogen atmosphere.

Measurements

Tin analysis was made by atomic absorption spectroscopy using a Perkin–Elmer Mod. 503 HGA equipment. Molar conductance was measured on a E 382 Metrohm A.C. conductivity bridge. The infrared spectra were recorded on a Perkin–Elmer Mod. 457 spectrophotometer. A Perkin–Elmer Mod. 402 was employed for the electronic spectra.

Results and Discussion

Table I lists analytical data, colours, melting points, reaction solvents, and molar conductance data of the complexes. These show a tin: ligand molar ratio 1 : 1; they are slightly soluble in the common solvents and melt with decomposition. Even if dry solvents are used and handlings are made under dry nitrogen, some of them when exposed to air are appreciably sensitive to moisture. This can be seen from the analytical data and i.r. spectra. On the other hand, all the water molecules are eliminated at 120° C.

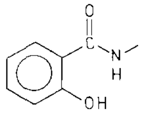
With the exception of HPIS in $SnPh(PIS)Cl_2 \cdot H_2O$, all the ligands are present in their protonated form. The behaviour as neutral donor molecule towards tin(IV) or organotin(IV) halides is quite usual for many other organic ligands.[10–12] This is consistent with the acceptor properties of tin(IV) derivatives. The deprotonation of the CONH group in $SnPh(PIS)Cl_2 \cdot H_2O$ is rather anomalous and not clear enough to explain in line with the existing literature. The same compound can also be obtained from the reaction of HPIS and Ph_2SnCl_2 in the presence of CH_3ONa.

Tin quantitative analysis was made by atomic absorption spectroscopy using a flameless spectrophotometer to avoid the sensitivity fluctuating with the structure of the compound.[13] The atomization temperature was 2660° C. Solutions of Ph_2SnCl_2 (1 ppm) in methanol and acetonitrile were used as standards for the organotin compounds. The choice of the solvents[14] for the conductivity measurements was made taking into account the poor solubility of the complexes in the common solvents. The Λ_M values, except that for $SnPh_2(HPIPOX)Cl_2$, indicate that they are non-electrolytes (Table I)[14]. The 157 ohm^{-1} cm^2 mol^{-1} value observed for $SnPh_2(HPIPOX)Cl_2$ is in agreement with a 2 : 1 electrolyte nature of the compound, which suggests the formulation $[SnPh_2(HPIPOX)]Cl_2$.

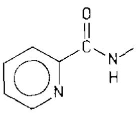
Infrared Spectra

Only the relevant vibrational bands of the complexes and the free ligands are reported in Table II with their relative assignments.

From a comparison of the free ligand spectra it can be observed that the $\nu(C{=}O)$ band occurs at higher frequencies in the ligands containing the



moiety than in those containing the



system. This fact can be explained by the presence of an O–H · · · N hydrogen bond in the former system, as observed in the HSIP molecule from the X-ray diffraction analysis.[15] An increase in the $\nu(C{=}O)$ frequency values is also observed for the following series: HSIP (1630 cm^{-1}), HPIS(1670 cm^{-1}), HPIP(1695 cm^{-1}), and HSIPOX(1650 cm^{-1}), HPIPOX(1675 cm^{-1}). All the spectra of the complexes, except that of $SnPh(PIS)Cl_2$

TABLE I. Analytical Data, Colours, Melting Points, Reaction Solvents, and Molar Conductance Data.

Complex	Sn%		C%		H%		N%		Cl%		M.P.	Colour	Solvent	Λ_M
	obs.	calcd.	obs.	calcd.	obs.	calcd.	obs.	calcd.	obs.	calcd.	(°C)			(ohm^{-1} cm^2 mol^{-1})
Sn(HSIP)$Cl_4 \cdot 4H_2O$	20.9	20.7	27.5	27.2	2.0	2.0	7.7	7.3	24.9	24.7	200	White	Ethanol	19 (CH_3CN)
Sn(HPIS)Cl_4	24.0	23.7	30.8	31.1	2.5	2.2	8.0	8.4	28.2	28.3	270	Pale yellow	Ethanol	19 (CH_3CN)
Sn(HPIP)$Cl_4 \cdot H_2O$	23.8	23.5	28.2	28.6	2.6	2.4	10.7	11.1	28.4	28.1	180	Yellow–orange	Ethanol	41 (CH_3CN) 37 (CH_3NO_2)
Sn(HSIPOX)Cl_4	21.4	21.1	32.3	32.1	3.0	2.7	7.7	7.5	25.0	25.2	235	Yellow	Ethanol	5 (CH_3CN)
Sn(HPIPOX)$Cl_4 \cdot 2H_2O$[a]	20.6	20.4	29.1	28.9	2.9	3.1	9.7	9.6	24.6	24.3	230	Yellow–orange	Ethanol	–
Sn(AIP)$Cl_4 \cdot H_2O$	19.1	19.5	37.7	37.5	3.0	2.8	11.3	11.5	23.0	23.3	160	Yellow	Ethanol	8 (CH_3NO_2)
$SnPh_2$(HSIP)Cl_2	20.4	20.3	51.0	51.3	3.8	3.6	6.9	7.2	12.3	12.1	170	White	Acetone	37 (CH_3OH)
SnPh(PIS)$Cl_2 \cdot H_2O$	22.9	22.6	43.2	43.5	3.0	3.3	7.9	8.0	13.8	13.5	130	Yellow–orange	Chloroform	5 (CH_3CN)
$SnPh_2$(HPIP)Cl_2	21.1	20.8	50.3	50.6	3.6	3.5	9.6	9.8	12.1	12.4	150	White	Benzene	18 (CH_3CN) 4 (CH_3NO_2)
$SnPh_2$(HSIPOX)Cl_2	18.7	18.4	50.2	50.3	4.2	3.9	6.2	6.5	11.3	11.0	220	Yellow	Ethanol	157 (CH_3OH)
$SnPh_2$(HPIPOX)Cl_2	18.9	18.8	45.9	45.8	4.0	3.8	9.0	8.9	11.4	11.3	200	Yellow	Ethanol	46 (CH_3OH)
$SnPh_2$(AIP)$Cl_2 \cdot 3H_2O$	16.6	16.3	50.9	51.2	3.8	4.3	9.8	9.6	9.8	9.8	160	Yellow–orange	Chloroform	22 (CH_3CN)

[a] Conductivity measurements were not possible as the complex is insoluble in the common solvents.

TABLE II. Main Vibrational Bands for the Ligands and the Complexes in the 4000–250 cm^{-1} Region.

Compound	$\nu(OH)_{water}$	$\nu(NH)$	$\nu(OH)$	Amide I $\nu(CO)$	Amide II $\nu(CN)$	$\nu(NN)$	$\nu(SnCl)$	$\nu(SnC)$	$\nu(SnO)$
HSIP		3240 m	2850 br 2720 br	1660 sh 1630 vs	1540 s	1035 m			
$Sn(HSIP)Cl_4 \cdot 4H_2O$	3420 s	3280 sh 3160 m	2800 br 2700 br	1648 vs	1550 vs 1540 vs	1040 m	330 sh 298 s		475 m
$SnPh_2(HSIP)Cl_2$		3220 s	2800 br	1628 vs	1545 vs 1535 vs	1035 m	302 m	260 m	460 m
HPIS		3270 m	2800 br 2700 br	1670 vs	1520 s	1040 m			
$Sn(HPIS)Cl_4$		3380 s	3140 m	1642 s	1550 vs	1050 m	360 sh 335 vs 310 vs		460 m
$SnPh(PIS)Cl_2 \cdot H_2O$	3450 m	–	?	1630 sh	1540 vs	1050 m	350 m	260 m	475 m
HPIP		3295 m		1695 sh 1675 s	1530 s 1510 s	1045 m			
$Sn(HPIP)Cl_4 \cdot H_2O$	3400 m	3300 m		1680 s	1530 s	1050 m	330 vs 300 vs		455 m
$SnPh_2(HPIP)Cl_2$		3240 m		1690 m	1520 vs	1040 w	300 m	265 m	455 m
HSIPOX		3350 m	2800 br	1650 vs	1550 s	1040 m			
$Sn(HSIPOX)Cl_4$		3240 sh	3520 s 3100 m	1650 s	1500 vs 1480 vs	1040 sh	350 m 315 s		435 m
$SnPh_2(HSIPOX)Cl_2$		3240 m	3420 m 3130 sh	1620 s	1520 vs 1490 vs	1040 m	335 m	280 m	440 m
HPIPOX		3180 m	3440 m 3400 sh	1675 vs	1525 vs	1040 m			
$Sn(HPIPOX)Cl_4 \cdot 2H_2O$	3520 s	3280 s	3420 s 3160 s	1670 br	1530 vs 1510 vs	1050 m	330 s 312 s		
$SnPh_2(HPIPOX)Cl_2$	–	3430 sh	3420 m 3130 sh	1710 w	1525 s	1050 m	–	295 m	
AIP		3240 m		1650 vs	–	1050 m	–		
$Sn(AIP)Cl_4 \cdot H_2O$	3500 br	3300 m	–	1670 vs	–	1040 w	315 m 290 s	–	–
$SnPh_2(AIP)Cl_2 \cdot 3H_2O$	3400 br	3330 s	–	1610 sh	–	1025 m	285 m	250 m	480 m

$\cdot H_2O$, are characterized by the presence of ν(NH) in agreement with the protonated form of the ligand.

With the only exceptions of $Sn(AIP)Cl_4 \cdot H_2O$ and $SnPh_2(HPIPOX)Cl_2$, all the complexes show CONH bands in agreement with a coordination through the oxygen atom, based on the lowering of the carbonyl stretching frequency.[7, 16–18] As is shown in Table II, the "amide I" band (mainly due to νC=O) is appreciably lowered (40–30 cm^{-1}) and "amide II" (mainly due to νC–N) is increased upon coordination to tin for $Sn(HPIS)Cl_4$ and $SnPh(PIS)Cl_2 \cdot H_2O$.

The same tendency for "amide I" was observed in $Sn(HSIPOX)Cl_4$ and $SnPh_2(HSIPOX)Cl_2$, but the "amide II" band is shifted to higher frequency. This fact can be explained by the coupling of the amide bands with those of the –N=C< bond in which the N atom is probably coordinated (as has been observed in $Zn(HPIP)X_2$ (X = Cl, Br))[7]. A smaller negative shift of "amide I" (15 cm^{-1}) and an almost unchanged position of the "amide II" are observed for $Sn(HSIP)Cl_4 \cdot 4H_2O$, $SnPh_2(HSIP)Cl_2$, $Sn(HPIP)Cl_4 \cdot H_2O$, $SnPh_2(HPIP)Cl_2$ and $Sn(HPIPOX)Cl_4 \cdot 2H_2O$, indicating a small coordinative interaction between tin and amide-oxygen atoms.

On the contrary, for $SnPh_2(HPIPOX)Cl_2$, the "amide I" band shifts to higher frequency while the "amide II" remains practically in the same position indicating the non-coordination of the –CON< group.

The "amide III" vibration could not be assigned owing to the complicated features of the spectra in the 1400–1200 cm^{-1} region.

For $Sn(AIP)Cl_4 \cdot H_2O$ and $SnPh_2(AIP)Cl_2 \cdot 3H_2O$, the infrared vibrational bands of –CON< and pyridine systems are quite similar to those observed in the spectra of $Cu(AIP)Cl_2$[4] and $Mn(AIP)Cl_2$[5] respectively. Therefore, it can be concluded that the ligand behaviour in the tin complexes is unchanged. Some small shifts to slightly higher frequencies in the 1600–1400 and 700–400 cm^{-1} regions for the pyridine vibrational bands are observed, suggesting the participation of the nitrogen atom in the coordination. This was also found in other complexes with the same ligands for which the X-ray analysis has established the coordination through the pyridine nitrogen atoms.[1, 2, 4, 5]

The spectra of all the complexes except $SnPh_2(HPIPOX)Cl_2$ are characterized by the stretching modes of tin–chlorine bond (Table II),[11, 19–23] which in $SnCl_4$ complexes are always multiple and appear at slightly higher frequency values. The lowering of the absorption frequency of ν(Sn–Cl) from the free Ph_2SnCl_2 to that of the complexes is indicative of an increased coordination number of the tin atom.[19]

In agreement with the ionic nature of two chlorine atoms, as deduced from conductivity data, $SnPh_2(HPIPOX)Cl_2$ does not show the tin–chlorine stretching vibration.

In addition to the ligand bands and the tin–chlorine vibrations, the complexes obtained from dichlorodiphenyltin show infrared absorptions characteristic of a σ-bonding phenyl ring in agreement with those found in the literature[24] and the tin–phenyl stretching modes (Table II).[12, 21–23] A *ca.* 450 cm^{-1} band occurs in the spectra of all the complexes in which the amide-oxygen

TABLE III. Electronic Absorptions of the Ligands and the Tin Complexes in Ethanol Solution.

Compound	λ(nm)[a]					
HSIP	219(4.42)		310(3.41)			
$Sn(HSIP)Cl_4 \cdot 4H_2O$	218(4.47)	303 sh	320(3.35)	350 sh	400 sh	
$SnPh_2(HSIP)Cl_2$	222(4.45)	303 sh	320(3.86)	350 sh	400 sh	
HPIS	225(4.53)	291 sh	302 sh	323(3.37)	333 sh	400 sh
$Sn(HPIS)Cl_4$	220(4.35)	290 sh	303 sh	320(3.52)	333 sh	400 sh
$SnPh(PIS)Cl_2 \cdot H_2O$	225(4.47)	290 sh	303 sh	320(3.55)	333 sh	395 sh
HPIP	235(4.11)		300(3.16)			
$Sn(HPIP)Cl_4 \cdot H_2O$	210(4.14)	273(5.31)				
$SnPh_2(HPIP)Cl_2$		270 sh	308(3.20)	390 sh		
HSIPOX	227(4.22)	298 sh	313(3.18)	350 sh		
$Sn(HSIPOX)Cl_4$	215(4.35)	255 sh		350 sh	405(2.98)	
$SnPh_2(HSIPOX)Cl_2$	220(4.27)	255 sh	315(3.33)	350 sh	410(2.85)	
HPIPOX	230(4.51)	301(3.35)	311 sh	342 sh		
$Sn(HPIPOX)Cl_4 \cdot 2H_2O$	220(4.60)	266(3.29)	273 sh	350(3.15)		
$SnPh_2(HPIPOX)Cl_2$	220(4.48)	300 sh	310(3.35)	345 sh	410 sh	
AIP	240(4.40)	310(3.45)	365 sh			
$Sn(AIP)Cl_4 \cdot H_2O$	233(4.87)	310(3.78)	350 sh			
$SnPh_2(AIP)Cl_2 \cdot 3H_2O$	265(4.72)	320(3.75)	370 sh			

[a] Log ε given in parentheses.

atom seems to be coordinated. This band is tentatively assigned to tin–oxygen stretching mode even if this attribution is quite uncertain owing to the spectrum complexity in the 600–300 cm^{-1} region and to the exceptionally wide range of frequency over which the ν(Sn–O) can occur.[25]

Electronic Spectra

The electronic absorption data of the ligands and the tin adducts in ethanol solution are reported in Table III. All the complexes of the same ligand show nearly similar spectra.

Since the six ligands have $>C=O$ and $>C=N-$ chromophore groups substituted in benzene or pyridine rings, the benzene bands are considerably red-shifted, as observed in other similar systems.[3,6,16]

The chelation effect causes small shifts of the electronic ligand transitions and the appearance of some new bands or shoulders. The high-wavelength bands (*ca.* 400 nm) can be due to charge-transfer transitions involving the tin atom.

Conclusions

In $Sn(HSIP)Cl_4 \cdot 4H_2O$, $SnPh_2(HSIP)Cl_2$, $Sn(HSIPOX)Cl_4$, $SnPh_2(HSIPOX)Cl_2$ and $SnPh_2(AIP)Cl_2 \cdot 3H_2O$ the vibrational bands of the ligands are very similar to those observed in the corresponding complexes with transition elements for which the X-ray analysis has previously established a terdentate ligand behaviour.[1,2,4,5] These results and the non-electrolyte nature of these complexes seem to suggest a seven-coordination around the tin atom. Nevertheless, no conclusive infrared proofs were reached about the coordination of tin by a second and a third basic ligand atom since no assignments of ν(C=N) and ν(C–O) (in PhOH derivatives) were attempted. In addition, a seven-coordination for tin is quite unusual and was rarely observed in connection with R_2Sn^{IV} derivatives[26–28] (examples concern mainly RSn^{IV} [29,30]). Thus, concluding on the coordinating behaviour of the ligands, the possibility of action as monodentate or as bridging bis-monodentate (mainly in the solid state) cannot be ruled out.[10,12,31,32]

We hope to achieve a better understanding of these configurations from a future structural X-ray investigation.

Acknowledgment

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