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Influence of the Donor Strength of the Ligands on the Structure of the Hexacoordinated Complexes of Tin(IV) Chloride. A Vibrational Spectroscopy Study

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Twenty three tin(IV) tetrahalide adducts with various monodentate ligands, cis- *and* trans- *$L_2 \cdot SnX_4$, were studied by IR and Raman spectroscopy at room temperature and above. The observed SnX stretching frequencies as well as the structure, are correlated with the donor number of the ligands. In some cases the basicity or the bulkiness of the ligand are not the prevalent factors in determining the structure of the complex.*

Introduction

The interaction of the Lewis' acid SnX_4 with a Lewis' base L leads normally to the formation of a complex with the composition $L_2 \cdot SnX_4$, in solution or in the solid state. The X-ray structures of few of these compounds *i.e.*, $(Cl_3PO)_2 \cdot SnCl_4$ [1], $(Cl_2SeO)_2 \cdot SnCl_4$ [2], $(Me_2SO)_2 \cdot SnCl_4$ [3] and $(MeCN)_2 \cdot SnCl_4$ [4] show a *cis*-configuration and, $(HMPT)_2 \cdot SnX_4$ (HMPT = hexamethylphosphorotriamide; X = Cl, Br) [5] and $(Et_3P)_2 \cdot SnCl_4$ [6] showed a *trans*- configuration.

The elucidation of the *cis*- or *trans*- configuration by infrared (IR) and Raman spectroscopy has been reported in the literature [7–10].

In the present work we discuss the influence of the donor number |Dn|, as defined by Gutmann [11], on the structure of the $L_2 \cdot SnX_4$ adducts, by the vibrational spectroscopy of the Y_2SnX_4 skeleton (Y = ligand donor atom).

Experimental

In our previous work [12] we reported the procedures for the preparation of the compounds.

The Raman spectra were obtained with the samples in a vacuum-sealed glass tube of 2 mm internal diameter. Above room temperature a specially designed cell was used [12] and the temperature was controlled with a flux of hot air. A Cary 82 spectrophotometer with an Ar ion laser of Spectra Physics model 165-08 was used to record the Raman spectra.

The IR spectra were obtained with a Perkin-Elmer model 180 spectrophotometer. Paraffin and fluor carbon oils were used to prepare the mulls and CsI and polyethylene windows were used to record the spectra.

The approximate description of the modes is presented in Table I; in Tables II and III the observed frequencies of the *cis*- and *trans*- compounds are given.

Discussion

The vibrational spectra in the low wavenumber region for the complexes can be interpreted assuming a C_{2v} or D_{4h} point group symmetry for the Y_2SnX_4 skeleton (Table I). Although for some of the compounds mentioned here the vibrational spectra were only sparsely reported in other works [10, 13–21], a detailed investigation in a series of compounds has not been done. It is then interesting to note that for the *cis*-Y_2SnCl_4 skeleton, the ν_1 and ν_2 appear in the Raman spectrum invariably with strong intensity at *ca.* 320 and at *ca.* 290 cm^{-1}, both with coincidence in the IR spectrum. For the *trans*-Y_2SnCl_4 skeleton the Raman spectrum normally shows a strong band at *ca.* 310 cm^{-1} (ν_1) and a medium one at *ca.* 250 cm^{-1} (ν_3) and the IR shows only one strong band at *ca.* 325 cm^{-1} (ν_5).

TABLE I. Approximate Description of the Stretching Modes of the Y_2SnX_4 Skeleton.

C_{2v}	A_1	B_1	B_2		
	ν_1		ν_5		str. SnX'^{a}
	ν_2	ν_4			str. SnX
	ν_3		ν_6		str. SnY
D_{4h}	A_{1g}	B_{1g}	A_{2u}	E_u	
	ν_1	ν_3		ν_5	str. snX
	ν_2		ν_4		str. SnY

[a] In the *cis*- complex, X' and X are the halogens at respectively, *cis*- and *trans*- positions in relation to the ligands.

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TABLE II. Stretching Frequencies (cm^{-1}) of the *cis*-Y_2SnX_4 Skeleton.

$L_2 \cdot SnCl_4$	Dn[a]	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
Cl_3PO	11.7	336	317	374	350	344	
PhCN	11.9	344	300	250	355	340	226
Cl_2SeO	12.2	336	287	426		332	
MeCN	14.1	336	301	205	357	346	192
$(CH_2O)_2SO$	15.3	333	302	403	341	333	
$(EtO)_2CO$[b]	16.0	331	295	440	344	320	400
Me_2CO	17.0	334	306	425	359	334	399
$MeCO_2Et$	17.1	336	302	408	345	332	403
$(MeO)_3PO$	23.0	328	294	380	333	333	360
$HCONMe_2$	26.6	328	282	421	340	314	416
$MeCONMe_2$	27.8	322	284	442	333	308	434
Me_2SO	29.8	321	275	480	334	303	476
Ph_3PO[c]	32.5	323	280	444	339	306	415
Me_3PO[c]	33.0	313	293	430	332	322	
$Me_2N(Cl)_2PO$		334	297	417	349	329	

[a] Dn = $-\Delta H SbCl_5 \cdot D$ ref. 11. [b] Ref. 22. [c] Ref. 23.

TABLE III. Stretching Frequencies (cm^{-1}) of the *trans*-Y_2SnX_4 Skeleton.

$L_2 \cdot SnCl_4$	Dn	ν_1	ν_2	ν_3	ν_4	ν_5
$PhCl_2PO$	18.5	320	382	257	378	334
$HCONMe_2$	26.6	313	419	249	424	335
$MeCONMe_2$	27.8	310	443	248	443	340
$(Me_2N)_2CO$	29.6	303	430	246	428	320
Me_2SO	29.8	304	481	248	486	328
C_5H_5N	33.1	306	160	247	227	323
$(Me_2N)_3PO$	38.8	310	519	245	523	323
$(Me_2N)_2ClPO$		321	484	255	482	332

The adducts of $HCONMe_2$, $MeCONMe_2$ and Me_2SO were isolated as both the *cis*- and *trans*- isomers for each ligand, with the *trans*- obtained from the *cis*- by an isomerization process in the solid state which was accelerated by an increase in temperature [12]. The other compounds melted or decomposed without any intermediate molecular structure transformation. Above room temperature, the Raman spectra showed that the melting or decomposition temperature increased for the complexes formed with higher Dn ligands. This observed tendency of the complex in relation to melting point with ligand basicity was also previously pointed out by Yeats *et al.* [24]. The Raman spectra of the fused compounds indicated for Cl_2SeO (Dn = 12.2), PhCN (Dn = 11.9) and $(CH_2O)_2SO$ (Dn = 15.3) some dissociation while, for $(MeO)_3PO$ (Dn = 23.0), we did not observe bands of the free acid or of the free ligand. We noted for $\{(MeO)_3PO\}_2 \cdot SnCl_4$ that the *cis*- configuration is maintained in the fused state which may reinforce the above observation about complex stability related with the Dn of the ligands, and advance also the influence of the Dn on the complex structure.

The influence of the Dn of the ligands is shown (Tables II, III) by the νMY which have a remarkable tendency to shift to higher frequencies as the Dn increase, but in this case we must consider that M–Y vibrations are normally highly coupled with other modes of the ligand and the skeleton Y_2SnX_4 [12–14]. The increase of the Dn is followed on the other side by the decrease of the νMX. This correlation is better observed for ν_1 of the *cis*-complex (Fig. 1) since it is the less coupled mode [12–14]. The observed trend is then due to the decrease of the SnCl bond stretching force constant and the consequent diminishing of the SnCl bond strength [15].

The stretching frequencies of the Y_2SnCl_4 skeleton are not well comparable when Y = O, N with Y = S, Se, P [25, 26], since besides the difference in terms of the kinetic energy matrix, the potential fields are also very different.

The application of the Zahrobsky's stereochemical model [27] for hexacoordinated *cis*-complex permitted us to conclude that, as the donor strength of the ligand increases the bond angle Y–Sn–Y is opened (see Table IV) and every bond angle approximates those of the octahedral ones in such a way that the

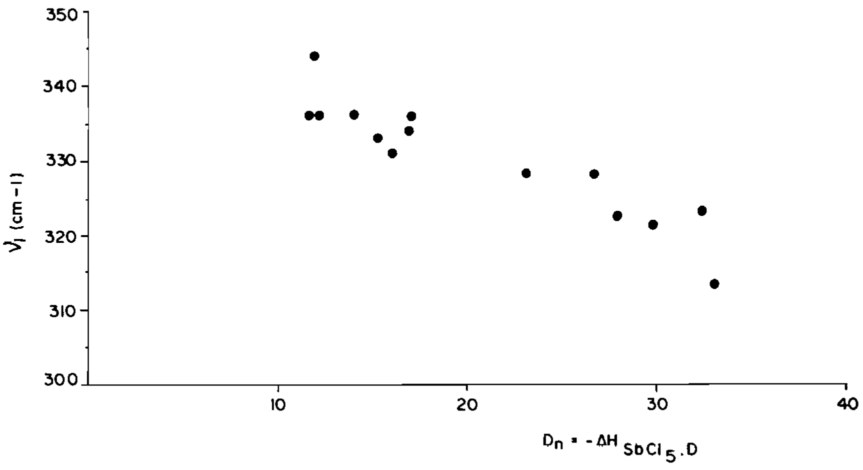

Fig. 1. Variation of the SnCl stretching frequencies of the *cis* complexes with the Dn of the ligands.

TABLE IV. Interbond Angles (degree) for *cis*-$Y_2 \cdot SnCl_4$ Skeleton.[a]

	Y–Sn–Y	X–Sn–X	X'–Sn–X'	Ref.
Cl_3PO	78.3	103.0	161.1	1
Cl_2SeO	81.9	100.1		2
MeCN	76.7	102.6	166.1	4
Me_2SO	84.0	97.6	172.7	3

[a] See footnote of Table I for the atom numbering.

energy difference between *cis*- and *trans*- isomers is decreased. We should note that the *trans*- configuration is attained if a relatively stronger Sn–Y bond is formed in order to compensate the instability caused by the higher overlap of the steric angles of the four halogens placed in the same plane [27]. In fact, we observe that the *trans*- complex is normally formed with ligands situated after the middle to the end of Gutmann's donicity scale. This fact is also consistent with the small *cis* → *trans* isomerization enthalpy in the solid state, *i.e.*, –0.24 kJ mol^{-1} for $(HCONMe_2)_2 \cdot SnCl_4$ [12] which ligand's Dn = 26.6.

The basicity of the ligand is not always the main factor which determines the geometry of the skeleton since bulky ligands can favor the *trans*- configuration [28] or the combined factors as observed by the series: *cis*- $(Cl_3PO)_2 \cdot SnCl_4$, *cis*-$(Me_2NCl_2PO)_2 \cdot SnCl_4$, *trans*-$\{(Me_2N)_2ClPO\}_2 \cdot SnCl_4$ and *trans*- $\{(MeN)_3PO\}_2 \cdot SnCl_4$. However, in the case of *cis*-$(Ph_3PO)_2 \cdot SnCl_4$ and *trans*-$(PhCl_2PO)_2 \cdot SnCl_4$, the reverse tendency is observed which may suggest that Dn or steric factors are not always prevalent.

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