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Addition Compound of Alkoxy Tin(IV) Trichloride with Some Phosphoryl and Amine-Oxide Ligands

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Addition compounds of alkoxy tin (IV) trichlorides, $Sn(OR)Cl_3$, (where $R = CH_3$, C_2H_5, C_3H_7 and C_2H_4Cl) with hexamethyl phosphoramide, triphenyl phosphine oxide, trimethyl phosphate, pyridine N-oxide, 8-hydroxyquinoline N-oxide and α,α'-dipyridyl N-N' dioxide have been prepared. All the complexes have 1:1 stoichiometry, are predominantly covalent and contain six coordinated tin due to coordination of the oxygen atoms of the ligand and the alkoxy group except for the dipyridyl dioxide complex in which alkoxy bridging is not present.

Introduction

The reluctance of the polymeric metal alkoxides[1] to form complexes with donor molecules has been attributed to the stronger basic nature of the alkoxy oxygen as compared to that of the donor atom of the ligand. However, incorporation of an electronegative atom like chlorine in the alkoxy group or in place of alkoxide group results in the reduction of polymerization[2,3] and this might induce the metal alkoxide to behave as an acceptor. This has been indicated by examining the acceptor properties of aluminium tris(2-chloroethoxide)[4] and alkoxy antimony(V) tetrachlorides.[5]

Although addition compounds of tin(IV) halides with some phosphoryl and amine-oxide ligands have been prepared, there appears to be no report of the formation of complexes with tin alkoxides or alkoxy tin(IV)halides. With a view to confirming the above mentioned possibility, we report the preparation of addition compounds of alkoxy tin(IV) trichlorides with these ligands.

Experimental Section

Solvents were purified by fractional distillation and the middle fractions were collected for use. Tin(IV) chloride was distilled in an all glass apparatus before use. Hexamethyl phosphoramide (BDH), pyridine N-oxide (Fluka) and trimethyl phosphate (BDH) were used after distillation. Triphenyl phosphine oxide (Fluka) was used as such. 8-hydroxy quinoline N-oxide and α-α'-dipyridyl N-N'dioxide were prepared by the method of Warren *et al.*[6] and Quagliano *et al.*,[7] respectively.

Methoxy-, ethoxy-, and n-propoxy tin(IV) trichloride monoalcoholates ($Sn(OR)Cl_3.ROH$) were prepared by a method described by Bradley *et al.*[8] while 2-chloro ethoxy tin(IV) trichloride monochloroethylate ($Sn(OC_2H_4Cl)Cl_3.C_2H_4ClOH$) was prepared as described by Paul *et al.*[9]

Complexes with hexamethyl phosphoramide were prepared by mixing hexamethyl phosphoramide with methanol solution of the alkoxide in nearly equimolar ratio of reactants and adding dry ether when solid compounds separated out. Similar procedure was adopted for the preparation of a complex of trimethylphosphate. In the case of pyridine N-oxide complexes, both the reactants were mixed as their solutions in methanol when a white precipitate appeared. However, the complexes of triphenyl phosphine oxide, 8-hydroxy quinoline N-oxide and α-α'-dipyridyl N-N'-dioxide were prepared by refluxing the mixture of the ligand with alcoholic solution of the alkoxide when the solid products precipitated out. There was no change in the composition of the complexes on changing the proportions of the reactants.

In all the cases, the complexes obtained were filtered in anhydrous condition, washed with dry ether and dried under vacuum.

A mixed ligand complex formulated as $Sn(OC_2H_5)Cl_3$.HMPA.pyridine was prepared by dissolving the HMPA complex in pyridine and precipitating the white solid by adding dry ether.

Results and Discussion

The reactions of the ligands (L) such as hexamethyl phosphoramide (HMPA), triphenyl phosphine oxide (TPPO), trimethyl phosphate (TMP), pyridine N-oxide (Py—O), 8-hydroxyquinoline N-oxide (HQ—O) and α-α'-dipyridyl N-N'dioxide (dipy—O2) with Sn(OR)-

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Table I. Complexes formulated as $\mathrm{Sn(OR)Cl_3}$. L where L stands for some phosphoryl and amine-oxide ligand.

Compound	Colour of solid	M.P. (°C)	(%) tin Found	(%) tin Caltd.	(%) chlorine Found	(%) chlorine Caltd.	Mol. Conc. × 10^3	Mol. Cond. $\mathrm{cm^2\,ohm^{-1}\,mole^{-}}$
1. $\mathrm{Sn(OCH_3)Cl_3}$. HMPA	White	267-68	36.15	36.11	32.15	32.40	0.6	2.4
2. $\mathrm{Sn(OC_2H_5)Cl_3}$. HMPA	White	254	25.99	26.40	22.50	23.70	4.6	0.4
3. $\mathrm{Sn(OC_2H_4Cl)Cl_3}$. HMPA	White	270	24.50	24.40	29.20	29.36	—	—
4. $\mathrm{Sn(OC_3H_7)Cl_3}$. HMPA	White	259	25.70	25.60	22.08	22.90	0.6	4.2
5. $\mathrm{Sn(OCH_3)Cl_3}$. TPPO	White	>290	21.90	22.20	—	—	0.1	2.1
6. $\mathrm{Sn(OC_2H_5)Cl_3}$. TPPO	White	272d	20.17	21.70	—	—	0.2	5.1
7. $\mathrm{Sn(OC_2H_4Cl)Cl_3}$. TPPO	White	270d	20.20	20.20	—	—	0.3	4.8
8. $\mathrm{Sn(OC_3H_7)Cl_3}$. TPPO	White	262d	20.70	21.20	—	—	0.06	1.2
9. $\mathrm{Sn(OC_2H_4Cl)Cl_3}$. TMP	White	—	26.10	26.70	30.70	31.80	—	—
10. $\mathrm{Sn(OCH_3)Cl_3}$. Py—O	Liquid White	240	32.90	33.80	30.90	30.30	0.9	1.3
11. $\mathrm{Sn(OC_2H_5)Cl_3}$. Py—O	White	254	31.90	32.50	29.30	29.10	0.8	0.6
12. $\mathrm{Sn(OC_2H_4Cl)Cl_3}$. Py—O	White	230	29.80	29.70	36.10	35.50	0.2	4.9
13. $\mathrm{Sn(OC_3H_7)Cl_3}$. Py—O	White	115	30.80	31.30	27.90	28.08	0.5	1.1
14. $\mathrm{Sn(OCH_3)Cl_3}$. HQ—O	Light Brown	>300	28.30	28.40	24.90	25.50	—	—
15. $\mathrm{Sn(OC_2H_4Cl)Cl_3}$. HQ—O	Light Brown	>290	25.30	25.50	29.10	30.50	3.2	2.8
16. $\mathrm{Sn(OCH_3)Cl_3}$. Dipy—$\mathrm{O_2}$	White	265d	25.50	26.70	23.90	23.98	1.3	9.0*
17. $\mathrm{Sn(OC_2H_5)Cl_3}$. Dipy—$\mathrm{O_2}$	White	258d	25.30	25.90	23.50	23.24	1.6	3.1*
18. $\mathrm{Sn(OC_2H_4Cl)Cl_3}$. Dipy—$\mathrm{O_2}$	White	242d	24.8	25.22	28.80	28.94	1.4	1.76*
19. $\mathrm{Sn(OC_3H_7)Cl_3}$. Dipy—$\mathrm{O_2}$	White	260d	26.90	27.03	23.40	23.90	0.34	22.0*
20. $\mathrm{Sn(OC_2H_5)Cl_3}$. HMPA. Pyridine	White	>300	21.80	22.50	19.60	20.05	—	—

* In DMSO and the others in nitrobenzene.

Table II. Major infrared frequencies of the complexes formulated as $\mathrm{Sn(OR)Cl_3}$. L

Phosphryl Compounds	ν(P=O)	ν(P—N) or ν(P—O—C) or (P—C)	$\nu(\mathrm{Sn}\overset{\mathrm{O}}{\diagup\searrow}\mathrm{Sn})$	ν(O→Sn)	ν(Sn—Cl)
HMPA	1205	985	—	—	
$\mathrm{Sn(OCH_3)Cl_3}$. HMPA	1170	995	510	390	320,315
$\mathrm{Sn(OC_2H_5)Cl_3}$. HMPA	1175	995	525	380	315,310
$\mathrm{Sn(OC_2H_4Cl)Cl_3}$. HMPA	1165	1000	510	395	310,295
$\mathrm{Sn(OC_3H_7)Cl_3}$. HMPA	1175	995	520	385	320,300
TPPO	1190	1445	—	—	—
$\mathrm{Sn(OCH_3)Cl_3}$. TPPO	1130	1465	510	360	320,305
$\mathrm{Sn(OC_2H_5)Cl_3}$. TPPO	1130	1465	505	380	315,305
$\mathrm{Sn(OC_2H_4Cl)Cl_3}$. TPPO	1110	1470	510	385	315,295
$\mathrm{Sn(OC_3H_7)Cl_3}$. TPPO	1125	1470	520	370	320,300
TMP	1275	1040	—	—	—
$\mathrm{Sn(OC_2H_4Cl)Cl_3}$. TMP	1230	1055	505	—	—

Amine oxide Compounds	ν(N—O)	δ(N—O)	ν(C—H) out ol plane def.	$\nu(\mathrm{Sn}\overset{\mathrm{O}}{\diagup\searrow}\mathrm{Sn})$	ν(O→Sn)	ν(Sn—Cl)
Py—O	1245	840	752	—	—	—
$\mathrm{Sn(OCH_3)Cl_3}$. Py—O	1195	830	775	490	380	310
$\mathrm{Sn(OC_2H_5)Cl_3}$. Py—O	1190	828	775	495	370—380	310,295
$\mathrm{Sn(OC_2H_4Cl)Cl_3}$. Py—O	1185	820	780	510	390	310,290
$\mathrm{Sn(OC_3H_7)Cl_3}$. Py—O	1190	825	770	530	380	310,300
HQ—O	1280	840	—	—	—	—
$\mathrm{Sn(OC_2H_4Cl)Cl_3}$. HQ—O	1240	825	—	510	370	310,295
Dipy—$\mathrm{O_2}$	1265,1255	852,840	745	—	—	—
$\mathrm{Sn(OCH_3)Cl_3}$. Dipy—$\mathrm{O_2}$	1235,1205,1185	835,820	770	[a]	390,365	310,290
$\mathrm{Sn(OC_2H_4Cl)Cl_3}$. Dipy—$\mathrm{O_2}$	1240,1205,1190	835,825	765	[a]	460,400,370	315,310
$\mathrm{Sn(OC_2H_4Cl)Cl_3}$. Dipy—$\mathrm{O_2}$	1240,1200,1180	825,815	775	[a]	440,395,370	310,295
$\mathrm{Sn(OC_3H_7)Cl_3}$. Dipy—$\mathrm{O_2}$	1245,1205	835,825	—	[a]	400,385,370	310

[a] Absence of such a band in this region.

$\mathrm{Cl_3}$. ROH (where R= $\mathrm{CH_3}$, $\mathrm{C_2H_5}$, $\mathrm{C_3H_7}$, and $\mathrm{C_2H_4Cl}$) produce addition compounds formulated as $\mathrm{Sn(OR)Cl_3}$. L. The results of analyses are given in Table I. These compounds are insoluble in most of the common organic solvents except for nitrobenzene and dimethylsulphoxide in which some of them have slight solubility. Low value of molar conductance of the complexes (Table I) in these solvents may be ascribed to their predominently covalent nature. The conductance of a number of Uni-Univalent electrolytes lies between 25-35 $\mathrm{cm^2\ ohm^{-1}\ mole^{-1}}$ in nitrobenzene[10] and 60-80 $\mathrm{cm^2\ ohm^{-1}\ mole^{-1}}$ in dimethylsulph-

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Table III.

Py–O	$SnCl_4 . 2Py–O$	$Sn(OCH_3)Cl_3 . Py–O$	Assignments
541	570	563	ligand
518	536	532	ligand
—	—	490	$\mathrm{Sn}\overset{\mathrm{O}}{\diagup\!\searrow}\mathrm{Sn}$
463	440	452	ligand
—	384	380	O→Sn
—	336	—	Sn—Cl
—	308	310	Sn—Cl
TPPO	$SnCl_4 . 2TPPO$	$Sn(OCH_3)Cl_3 . TPPO$	Assignment
—	—	510	$\mathrm{Sn}\overset{\mathrm{O}}{\diagup\!\searrow}\mathrm{Sn}$
460 m	456 m	455 m	ligand
448 m	446 m	448 m	ligand
403 w	410 m	—	ligand
293 m	325 sh	390 s	O→Sn
—	337 s	—	
—	320 s	320 s	Sn—Cl
—	298 s	305	Sn—Cl

oxide.[11] The molecular weight of these complexes could not be determined due to their insufficient solubility in these solvents.

The P=O stretching frequency in the phosphoryl complexes is found to have decreased as compared to those in the free ligand (Table II) which may be due to the coordination of the phosphoryl oxygen[12,13] atom to tin. The P–C and P–O–C stretching frequencies in TPPO and TMP respectively and the P–N frequency in HMPA shifts to higher spectral region which further supports the above mode of coordination.[12,13] Similarly examination of the spectra of amine-oxide ligands (Table II) reveals the lowering of N–O stretching and bending frequencies while the C–H stretch (out of plane deformation) shifts to the higher frequencies. This may also be due to the coordination of oxygen atom of these ligands[14,15] to tin. Un-coordinated dipy–O_2 have two bands[7] corresponding to each of the N–O stretching and bending modes and these bands shift to lower frequencies on complex formation. This indicates that dipy–O_2 acts as a bidentate ligand.

In contrast to the formation of 1:1 addition compounds by 8-hydroxy quinoline[16] or pyridine,[16] their oxides form only 1:1 complexes. In the monodentate ligand complexes, the coordination number of tin might be five as is known for corresponding 1:1 complexes of TPPO with Me_3SnCl.[17] The other possibility is that tin may attain hexa-coordination where the complexes might acquire dimeric framework analogous to the parent monoalcoholate of these alkoxides[8] and some compounds of alkoxy titanium(IV) halides.[1,2] The evidence for the dimeric framework is provided by the presence of a strong intensity band present at 480-530 cm^{-1} region which is not present in the ligands but is present in $Sn(OR)Cl_3 . ROH$ and might be assigned to $\mathrm{Sn}\overset{\mathrm{O}}{\diagup\!\searrow}\mathrm{Sn}$ vibrations.[18] The fact that such a band is also absent in the adducts of tin(IV), compounds not involving alkoxy group with TPPO[13] and Py–O[15] favours the above assignment and this is obvious from a comparison of the spectra as given in Table III.

A further support is provided by the fact that such a band is absent in the 1:1 complexes with dipy-O_2 and also in 1:2 complexes with 8-hydroxy quinoline[16] or pyridine.[16] This might be due to the fact that in these complexes alkoxy bridging is absent since tin attains hexa-coordination without this autocomplexation.

All the compounds have strong intensity bands in 290-320 frequency region (Table II) and this is the region where Sn–Cl vibrations of $SnCl_6^{2-}$ occur[19] (ν_3 for $(NH_4)_2$ $SnCl_6$ is at 312 cm^{-1}).[19] The spectra of solid adducts of HMPA closely resemble their spectra in solution in nitrobenzene and the position of bands corresponding to Sn–Cl and $\mathrm{Sn}\overset{\mathrm{O}}{\diagup\!\searrow}\mathrm{Sn}$ are not altered much, which is indicative of the similar structure in both the solid and solution state.

Apart from the Sn–Cl and the ligand vibrations in the CsBr region, the complexes show some additional bands at 370-440 cm^{-1} region which may be assigned to O→Sn vibrations[15,20] and these bands are absent in analogous compounds with pyridine or dipridyl since N→Sn vibrations are known to absorb below 250 cm^{-1}. Assignment of the bands corresponding to Sn–Cl and O→Sn vibrations agrees well with the previous work (Table III) in the complexes of some of these ligands with tin(IV) chloride.[13,15]

Mixed Ligand Complex. A complex formulated as

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$Sn(OC_2H_5)Cl_3$. HMPA. pyridine has also been prepared. The infra-red spectrum of this complex shows the bands corresponding to coordinated pyridine[21,22] at 1630, 1600 cm^{-1} ν(C$\overset{\dots}{=}$C and C$\overset{\dots}{=}$N) and the ring vibrations at 1005, 620 and 415 cm^{-1} along with the vibrations due to coordinated HMPA. Of course the bands present in HMPA complex which is assigned to $\mathrm{Sn}\diagup^{\mathrm{O}}\searrow\mathrm{Sn}$ vibrations is absent which suggests the possible absence of alkoxy bridging in this complex. This might be mainly due to the fact that tin in HMPA complex prefers coordination from nitrogen atom of pyridine than to self complexation through alkoxy bridging.

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