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# Co-ordination Compounds of Acetamide and its Substituted Derivatives with Diphenyltin Dihalides

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*Twelve new thermally stable molecular adducts of the general formula* $(C_6H_5)_2SnX_2$ *nL (X = Cl, Br or I, n = 1 or 2 and L = acetamide, N-methylacetamide, dimethylacetamide, diethylacetamide or diphenylacetamide) have been isolated in the crystalline state and characterised The infrared data on these penta or hexa co-ordinated adducts indicate coordination from the oxygen atom of the Lewis base to the tin atom Possible stereochemistry of the complexes is suggested*

## Introduction

Recently, some molecular adducts of organotin halides with carbonyl donors, particularly amides, have been synthesised and their structure investigated through infrared, Raman, nuclear magnetic resonance and Mossbauer spectroscopy[1–8] It has been concluded that in all the cases, coordination occurs through the oxygen atom of the carbonyl group 1 2 complexes mostly possess distorted octahedral structure, while 1 1 adducts are trigonal bipyrimidal in shape Petrosyn *et al* [9–11] have examined the effect of organic solvents on the rate and mechanism of organometallic reactions through Mossbauer and nuclear quadrupole resonance spectroscopy and observed strong intermolecular interaction between organotin halides and the electrons

While several reports have appeared on the complexes of N,N'-dimethylacetamide with dialkyl and trialkyltin derivatives[4–8], the corresponding complexes involving aryltin moiety have not received attention of the workers We, therefore, wish to report the isolation and characterisation of some new complexes of diphenyltin dihalides with acetamide (A), N-methylacetamide (NMA), dimethylacetamide (DMA), diethylacetamide (DEA) and diphenylacetamide (DPA) The probable structure is discussed, on the basis of the infrared spectra

## Experimental

Diphenyltin dihalides were prepared as reported[12] and the laboratory grade amides were used after purification by conventional methods

Melting points were determined on an electrically operated instrument and elemental analyses were carried out on a semi micro scale at the Central Drug Research Institute, Lucknow, India The infrared spectra were recorded as KBr/Nujol on a Perkin–Elmer spectrophotometer model 521 The molecular weight of typical complexes was determined cryoscopically in benzene using a Beckmann thermometer with an accuracy of 01°C and the molecular conductance of $10^{-3} M$ solution in anhydrous nitrobenzene was measured at 30°C by Philip's Magic Eye, model PR 9500 conductivity bridge using a dip type conductivity cell

### *Preparation of Adducts*

In a typical reaction, 2 mmol of diphenyltin dihalide in carbon tetrachloride or petroleum ether was mixed with an appropriate quantity of a Lewis base in the same solvent The mixture was stirred for an hour and the precipitated adduct was filtered, washed, recrystallised and dried *in vacuo*

### *Ligand Displacement Reaction*

The reaction of the $Ph_2SnCl_2$ 2L adducts with a few strong donors (L') such as 1,10-phenanthroline, 2,2'-bipyridyl, dimethylsulfoxide and pyridine N-oxide was studied

In a typical reaction, 1mmol of the adduct was stirred with a solution of an excess of a strong donor (L') in ethanol or diethylether at room temperature for two hours The solid product obtained, was filtered, washed, vacuum dried and identified

## Results and Discussion

The experimental data on the newly prepared molecular adducts are summarised in Table I All complexes

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TABLE I. Experimental Data for Adducts of Diphenyltin Dihalides.

| | Adduct | M.p. (° C) | Analysis (%), Found (Calcd.) | | | |
|---|---|---|---|---|---|---|
| | | | Sn | C | H | N |
| 1 | $Ph_2SnCl_2 \cdot 2A$ | 101–104 | 26.13<br>(25.70) | 41.50<br>(41.58) | 4.31<br>(4.33) | 6.44<br>(6.06) |
| 2 | $Ph_2SnBr_2 \cdot 2A$ | 98–100 | 21.62<br>(21.55) | 34.74<br>(34.84) | 3.50<br>(3.63) | 5.05<br>(5.08) |
| 3 | $Ph_2SnCl_2 \cdot NMA$ | 62 | 28.32<br>(28.48) | 43.41<br>(43.19) | 4.41<br>(4.07) | 3.22<br>(3.35) |
| 4 | $Ph_2SnCl_2 \cdot 2NMA$ | 66– 67 | 24.64<br>(24.23) | 44.24<br>(44.10) | 4.81<br>(4.90) | 5.73<br>(5.71) |
| 5 | $Ph_2SnCl_2 \cdot DMA$ | 96 | 27.16<br>(27.55) | 44.84<br>(44.58) | 4.23<br>(4.41) | 3.25<br>(3.24) |
| 6 | $Ph_2SnCl_2 \cdot 2DMA$ | 100–101 | 22.71<br>(22.92) | 46.74<br>(46.35) | 5.30<br>(5.41) | 5.72<br>(5.40) |
| 7 | $Ph_2SnBr_2 \cdot DMA$ | 83– 85 | 23.26<br>(22.84) | 37.15<br>(36.94) | 3.55<br>(3.65) | 2.60<br>(2.69) |
| 8 | $Ph_2SnI_2 \cdot DMA$ | 80– 81 | 19.64<br>(19.47) | 30.76<br>(31.28) | 3.54<br>(3.09) | 1.85<br>(2.28) |
| 9 | $Ph_2SnCl_2 \cdot 2DEA$ | 76– 78 | 21.01<br>(20.69) | 50.02<br>(50.20) | 6.26<br>(6.27) | 4.81<br>(4.88) |
| 10 | $Ph_2SnBr_2 \cdot 2DEA$ | 68– 72 | 18.12<br>(17.91) | 43.07<br>(43.45) | 5.51<br>(5.43) | 4.53<br>(4.22) |
| 11 | $Ph_2SnCl_2 \cdot DPA$ | 105–106 | 20.91<br>(21.39) | 55.80<br>(56.06) | 4.11<br>(4.14) | 2.55<br>(2.52) |
| 12 | $Ph_2SnBr_2 \cdot DPA$ | 109–110 | 19.01<br>(18.42) | 48.62<br>(48.43) | 3.53<br>(3.57) | 2.20<br>(2.17) |

are white crystalline solids, soluble in common organic solvents. They are thermally stable and do not decompose when heated at their melting point for several hours. Their molecular weight determined in freezing benzene is considerably lower than their formula weight suggesting a significant dissociation in solution. The molar conductance of $10^{-3} M$ solution in nitrobenzene at 30° C is observed in the range 0.64–1.11 $ohm^{-1}$ $cm^2/mol$ while it is expected to be between 20–30 $ohm^{-1}$ $cm^2/mol$ for 1:1 electrolyte[13]. The data thus indicate non-electrolytic behaviour of the complexes. The isolation of 1:1 or 1:2 complexes appears to be largely governed by steric factors and depends on the relative size of the donor molecule and that of the halogen of the Lewis acid. Accordingly, DPA, a large sized base yields only complexes of 1:1 stoichiometry, while A, a comparatively smaller molecule prefers to give 1:2 adducts. NMA and DMA give both 1:1 and 1:2 adducts with diphenyltin dichloride, while DMA with corresponding bromide and iodide yields only 1:1 product. The electronegativity or the halide group bonded to the tin atom also appears to affect the stability of the adducts in the crystalline state. Thus if the number of adducts isolated is taken as a measure of the stability of the complexes the following order is apparent: $Cl > Br > I$

The melting point, elemental analysis and infrared spectra of the products of the reaction between $Ph_2SnCl_2 \cdot 2A$ and four strong donor bases were almost identical to the corresponding authentic samples (Table II). The interaction of the newly prepared adducts with these strong donors therefore results in complete displacement of the amide molecule.

### *Infrared Spectra*

The infrared absorptions of diagnostic value of the Lewis bases and their adducts in the range 2000–200 $cm^{-1}$ are summarised in Table III.

### *Ligand Absorption*

The N–H stretching absorptions in the spectra of primary (A) and secondary (NMA) amides and their adducts have been identified around 3300 $cm^{-1}$ but are not tabulated as they are little affected on complexation. The amide II band possessing a major contribution from the N–H deformation mode is also insensitive to complexation which indicates that the lone pair of electrons on the nitrogen atom of the bases does not take part in coordination.

On the other hand a significant negative shift of the amide I band associated with C=O stretching frequency and a positive shift of $\nu$C–N in the spectra of all the complexes as compared to that in the free base indicate coordination from the oxygen atom of the carbonyl group to the tin atom. As a result of such coordination the double bond character of the carbonyl group

TABLE II. Experimental Data on the Product of Reaction between $Ph_2SnCl_2 \cdot 2A$ and Strong Ligands (L′).

| L′ | Product | M.p. (° C) obsd. (reported) | Analysis (%), Found (Calcd.) | | | |
|---|---|---|---|---|---|---|
| | | | Sn | C | H | N |
| Phen | $Ph_2SnCl_2 \cdot$ Phen | 259–60<br>(261) | 22.66<br>(22.66) | 54.84<br>(54.99) | 3.26<br>(3.43) | 5.40<br>(5.34) |
| Bipyl | $Ph_2SnCl_2 \cdot$ Bipy | 237–39<br>(239–40) | 23.70<br>(23.75) | 52.76<br>(52.83) | 3.71<br>(3.60) | 5.42<br>(5.60) |
| DMSO | $Ph_2SnCl_2 \cdot$ 2DMSO | 133–35<br>(135) | 23.55<br>(23.74) | 38.61<br>(38.40) | 4.62<br>(4.40) | |
| PyO | $Ph_2SnCl_2 \cdot$ 2PyO | 170–73<br>(175) | 22.41<br>(22.29) | 49.82<br>(49.46) | 3.63<br>(3.74) | 4.99<br>(5.24) |

TABLE III. Infrared Absorption Frequencies ($cm^{-1}$) of the Lewis Bases and Their Adducts with Diphenyltin Dihalides.

| Compound | $\nu$C=O | $-\Delta\nu$C=O | $\nu$C–N contiguous to C=O | $\nu$N–C contiguous to $CH_3$ | $\nu$Sn–O | $\nu$Sn–X | $\nu$Sn–Ph | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | asym. | sym. |
| A | 1675 vs | | 1342 s | | | | | |
| 1[a] | 1647 vs | 28 | 1382 m | | 355 w | 267 m | 290 m | 230 m |
| 2 | 1646 vs | 29 | 1386 s | | 345 w | | 281 m | 236 m |
| NMA | 1670 vs | | 1300 m | 1170 m | | | | |
| 3 | 1640 vs | 30 | 1315 m | 1180 m | 340 m | 260 m | 288 m | 237 m |
| 4 | 1635 vs | 35 | 1310 m | 1175 m | 345 m, br | 256 m | 282 m | 232 m |
| DMA | 1633 vs | | 1265 s | 1190 s | | | | |
| 5 | 1590 vs | 43 | 1300 m | 1205 m | 350 m | 275 m | 285 m | 240 m |
| 6 | 1592 vs | 41 | 1307 m | 1200 s | 355 m | 270 m | 283 m | 235 w |
| 7 | 1593 vs | 40 | 1299 m | 1190 m | 340 w, br | | 295 m | 242 m |
| 8 | 1591 vs | 42 | 1299 m | 1195 s | 350 m, br | | 278 m | 232 m |
| DEA | 1636 vs | | 1276 s | 1171 m | | | | |
| 9 | 1578 vs | 58 | 1333 m | 1176 m | 335 m, br | 267 m | 278 m | 235 m |
| 10 | 1574 vs | 62 | 1331 m | 1180 w | 342 m, br | | 286 m | 240 m |
| DPA | 1678 vs | | 1320 vs | 1145 m | | | | |
| 11 | 1602 vs | 76 | 1348 m | 1156 m | 340 s | 282 s | 271 m | 243 m |
| 12 | 1606 vs | 72 | 1360 s | 1156 w | 345 m | | 277 m | 250 m |

[a] Serial numbers in column 1 refer to complexes in Table I; s = strong, v = very, m = medium, w = weak, br = broad.

decreases with consequent lowering of $\nu$C=O, while the C–N bond attains a partial double bond character and absorbs at a higher frequency. The complexes of secondary and tertiary amides also show a slight positive shift of the N–C stretching mode.

The extent of lowering of the carbonyl stretching frequency on complexation has been utilised as a measure of the donor ability of amides towards Lewis acids[14–16]. On the basis of the data on this vibration in the present investigation, the following order may be suggested for the relative donor ability of acetamide and its substituted derivatives towards diphenyltin dihalides: DPA > DEA > DMA > NMA > A

The apparent order is consistent with the electron releasing tendency of the organic groups attached to the nitrogen atom of the acetamide. The exceptionally large negative shift of the $\nu$C=O in DPA complexes observed, may however, be attributed to the greater availability of the electrons on the carbonyl group from the aromatic ring system as observed and explained by Krishnamurthy and Soundarajan[17].

### *Metal–Ligand Atom Absorptions*

An absorption at 345 ± 10 $cm^{-1}$ in the spectra of all the adducts but absent in the spectra of the parent Lewis acids and uncoordinated bases, has been assigned to the Sn–O stretching mode on the basis of the reported data[1, 18, 19] which strongly supports donation of electrons from the oxygen atom of the carbonyl group. This absorption has, however, been identified at 200 $cm^{-1}$ for $Me_2SnCl_2 \cdot DMF$[2], and at 272 $cm^{-1}$ for $Ph_2SnCl_2 \cdot 2DMF$[3] which is apparently too low. One of us has recently recorded the infrared and Raman spectra of a number of adducts of diphenyltin derivatives with various oxygen donors and has identified this absorption in the suggested range[20]. The relative position of this absorption in the adducts of different bases is very close to each other and does not permit confirmation of the order of the relative donor strength of the bases determined on the basis of the negative shift in the C=O stretching vibration.

The spectra of diphenyltin dihalides show two distinct absorptions due to asymmetric and symmetric stretchings of the Sn–X bond ($\nu$Sn–Cl = 364, 356; $\nu$Sn–Br = 252, 241; $\nu$Sn–I = 204–196, 186–176 cm$^{-1}$)[21]. In the spectra of the adducts of diphenyltin dichloride, however, only one band assignable to $\nu$Sn–Cl could be identified at about 90–100 cm$^{-1}$ lower than that in the spectrum of the Lewis acid. A similar lowering of $\nu$Sn–X on increase in the coordination number of tin has been reported by previous workers[22,23]. In the adducts of diphenyltin dibromide and diiodide, $\nu$Sn–Br and $\nu$Sn–I are, therefore, expected to shift beyond the recorded range of the spectra. The symmetric Sn–Cl stretching vibration identified by Liengme *et al.*[3] in the spectra of some $Ph_2SnCl_2 \cdot 2L$ complexes around 200 cm$^{-1}$ is questionable since an out of plane ring bending is reported to appear almost at the same position[24]. It is, therefore, difficult to make unambiguous assignment of $\nu_{symm}$Sn–Cl strctching mode of vibration.

The absorptions due to asymmetric and symmetric stretchings of Sn–Ph linkage in Lewis acids at 275 ± 5 and 240 ± 5 cm$^{-1}$ respectively are almost insensitive to complexation[22,23]. Precisely speaking, these are associated with the aromatic ring vibrations, designated by *t* and *t′* by Whiffen[24] but since they are highly sensitive to the mass of the substituted metal atom and involve a major contribution of Sn–Ph bond, they have generally been recognised as asymmetric and symmetric stretchings of the Sn–Ph linkage.

The presence of two Sn–Ph and onc Sn–Cl stretching vibrations in the hexa-coordinated complexes ($Ph_2SnCl_2 \cdot 2L$) may be interpreted as being due to two phenyl groups in the *cis* position and the two chlorine atoms lying *trans* to each other. But in view of the Mössbauer spectroscopic data reported by other workers[3], a structure having a distorted octahedron in which the two chlorine atoms lie in *cis* position and the two phenyl groups *trans* to each other cannot be ruled out, particularly when there is strong likelihood of the other Sn–Cl stretching absorption being masked by the out-of-plane ring bending mode.

The complexes of 1 : 1 stoichiometry ($Ph_2SnCl_2 \cdot L$) are apparently penta-coordinated and may posses a trigonal bipyramidal geometry in which the two phenyl groups and a halogen atom are likely to occupy equatorial position while one Cl and L are *trans* to each other in the apical position as suggested by Liengme *et al.*[3]

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