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COORDINATION COMPOUNDS OF DIMETHYLFORMAMIDE WITH DIARYLTIN DIHALIDES

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SUMMARY

Eight new molecular addition compounds of the type $R_2SnX_2 \cdot 2$ DMF (R = phenyl, *o*-tolyl, *p*-tolyl, or benzyl and X = Cl, Br, or I) have been prepared. The infrared spectra indicate coordination of the ligand molecule to the tin atom via oxygen.

INTRODUCTION

Dimethylformamide (DMF) has been widely used as a Lewis base and its molecular adducts with several metal halides[1–10], oxyhalides[11], perchlorates[12,13], and nitrate[14] have been reported. Various spectral studies on such adducts indicate that the ligand is bonded to metals through oxygen atom of the carbonyl group. However, studies of the adducts of DMF involving organometallic cations such as alkyllead and alkyltin are of recent origin. We have, therefore, investigated the interaction of this Lewis base with a number of diaryltin dihalides, and prepared eight new complexes of the type $R_2SnX_2 \cdot 2$ DMF (R = phenyl, benzyl, *o*-, *m*- or *p*-tolyl; X = Cl, Br or I). The compounds have been characterised and their infrared spectra studied.

EXPERIMENTAL

The complexes were prepared by the interaction of diaryltin dihalides with dimethylformamide.

In a representative experiment, 5 mmoles of diaryltin dihalides were dissolved in excess of DMF (20 mmole) by gradual heating on water bath. The solution was then allowed to stay overnight in a refrigerator, and a white crystalline complex separated. It was recrystallized from carbon tetrachloride and dried in vacuum.

When the above reaction was carried out using diethyl ether as the solvent, identical products were obtained. Variation of the molar ratio of the reactants also had no effect on the stoichiometry of the products. The melting points, molecular weights in freezing benzene and the analytical data of the hitherto unreported complexes are summarized in Table 1.

The complexes are white crystalline solids, soluble in common organic solvents such as benzene, chloroform, ether etc. They are thermally stable and do not decompose when heated for several hours at their melting points. The complexes are only

TABLE 1

EXPERIMENTAL DATA FOR $R_2SnX_2 \cdot 2DMF$

R	X	M.p. (°C)	Analytical data, found (calcd.)				
			C (%)	H (%)	N (%)	Sn (%)	Mol.wt.
Phenyl	Cl	71	44.4 (44.1)	4.7 (4.8)	5.1 (5.7)	23.6 (24.2)	315 (490)
Phenyl	Br	68	37.5 (37.4)	4.0 (4.1)	4.8 (4.8)	19.8 (20.5)	
Phenyl	I	81	32.5 (32.1)	3.7 (3.6)	4.7 (4.1)	16.5 (17.6)	201 (673)
o-Tolyl	Cl	95	46.7 (46.3)	5.1 (5.4)	5.0 (5.4)	22.3 (22.9)	278 (518)
o-Tolyl	Br	97	39.4 (39.5)	4.0 (4.6)	4.5 (4.6)	19.7 (19.6)	
p-Tolyl	Cl	73	45.9 (46.3)	5.5 (5.4)	5.2 (5.4)	22.3 (22.9)	251 (518)
p-Tolyl	Br	63	39.0 (38.5)	4.2 (4.6)	5.2 (4.6)	19.7 (19.6)	
Benzyl	Cl	68				22.3 (22.9)	290 (518)

slightly hygroscopic, except for dibenzyltin dichloride 2 DMF, which is highly sensitive to moisture. A complete hydrolysis of the compounds gives diaryltin oxide as the final product. The cryoscopically determined molecular weights of the complexes in benzene show abnormally low values as compared to those calculated from the molecular formula thus indicating a significant dissociation in solution. However, the conductance measurement of a $10^{-4}\,M$ solution in nitrobenzene indicated the absence of ionic species.

The interaction of the complexes with other Lewis bases stronger than DMF such as 1,10-phenanthroline, 2,2'-bipyridine, dimethyl sulphoxide, and *N*,*N*-dimethylacetamide was investigated. It has been found that complete substitution of the ligand takes place and the donor ability of DMF towards diaryltin dihalides is weak compared with the other Lewis bases examined.

The infrared spectra of DMF and its complexes with diaryltin dihalides were recorded in the region 4000–650 cm^{-1} using Perkin–Elmer infrared cord spectrophotometer model 337. Some of the samples were also examined in the range 650–200 cm^{-1} using Perkin–Elmer 521 model. The important absorption frequencies associated with various modes of variations are summarized in Table 2.

The most significant absorption in the spectra of these compounds is the carbonyl stretching mode located as a strong band at 1666 cm^{-1} in pure DMF. In the spectra of the complexes, however, it is located at 1645 ± 5 cm^{-1} indicating a negative shift of 25 ± 5 cm^{-1}. On the other hand absorptions due to C–N (contiguous to C=O) and N–C (contiguous to CH_3) stretching vibrations in the free ligand show a positive shift on complexation. These spectral changes show coordination via the oxygen atom of the amide[3,16].

Six significant absorptions have been located in the CsBr region, two of these are associated with the ligand while the other four involve vibrations of the metal

TABLE 2

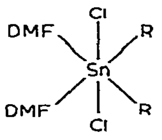
ABSORPTION FREQUENCIES (cm^{-1}) OF DMF AND $R_2SnX_2 \cdot 2DMF$

Assignment	DMF	Phenyl			*o*-Tolyl		*p*-Tolyl		Benzyl Cl
		Cl	Br	I	Cl	Br	Cl	Br	
(C=O)	1666 vs	1640 vs	1637 vs	1640 vs	1647 vs	1638 vs	1647 vs	1639 vs	1638 vs
CH_3	1383 m	1371 s	1365 m	1365 vs	1373 s	1353 s	1378 s	1360 s	1372 s
(C=N)[a]	1267 m	1311 m		1315 s	1280 s	1275 s	1318 s	1307 m	
(N–C)[b]	1103 vs	1115 s	1110 m	1127 vs	1107 m	1112 vs	1119 vs	1103 m	1115 vs
(N–C=O)	662 vs	688 s	682 vs	682 s	677 s	676 vs	678 vs	678 s	680 vs
Ligand band	361 s	380 m	384 vs	378 s	383 m		385 vs		
Sn–O		350 w	350 w	350 w	350 w		348 sh		
		342 w	340 w		344 w				
Sn–Cl		275 m			274 m		265 m		
Sn–Ph asymm.		287 m	285 m	285 m	289 m		275 sh		
Sn–Ph symm.		245 w	235 w	230 w	244 m				

[a] Contiguous to C–O. [b] Contiguous to CH_3.

atom. Thus DMF absorbs strongly at 662 cm^{-1} due to a deformation mode arising out of a major contribution from O=C–N. On coordination from the oxygen atom this absorption is shifted to higher frequency region and appears at 682±6. Another ligand absorption at 361 in pure DMF appears in the spectra of the complexes at 382±4, also showing a distinct positive shift.

The Sn–Cl stretching frequency has been identified in the spectra of the tetracoordinated diphenyl-, di-*o*-tolyl-, and di-*p*-tolyltin chlorides at 364, 359 and 340 cm^{-1} respectively. On complexation, the corresponding absorptions occur at 275, 274, and 265 cm^{-1} and the significant lowering of the absorption frequency is characteristic of increase in the coordination number of the metal atom[18,19]. Two absorptions of medium to weak intensity in the range 275–289 cm^{-1} and 230–245 cm^{-1} are assigned to asymmetric and symmetric tin–aryl stretchings. Since two Sn–Ar and only one Sn–Cl stretching absorptions are identified in the spectra of the hexacoordinated complexes, it may be concluded that the two aryl groups occupy *cis* position while the two chlorine atoms are *trans* to each other. The structure may thus be represented as



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