Indian Journal of Chemistry
Vol. 23A, January 1984, pp. 75-76

Complexes of Triphenyltin Pseudohalides with Amides

(Mrs) RAJESHWARI RUPAINWAR* & B D PANDEY†
Chemistry Section, Mahila Mahavidyalaya, BHU, Varanasi 221 005

Received 18 *April* 1983; *revised and accepted* 28 *September* 1983

Ten new complexes of triphenyltin pseudohalides of the general formula $Ph_3SnX.L$, where X = NCO or NCS and L = dimethylformamide (DMF), diphenylformamide (DPF), dimethylacetamide (DMA), diphenylacetamide (DPA) or dimethyloxamide (DMO), have been prepared and characterised. The complexes have been assigned five coordinate geometry on the basis of analytical, conductance, molecular weight and IR spectral data; the dimethyloxamide adduct is, however, six coordinated. Antibacterial and antifungal properties of the compounds have been also tested.

Pentacoordinate adducts of some triorganotin compounds with dimethylformamide (DMF) have been prepared by Drago *et al.*[1] who assigned trigonal-bipyramidal structures to the complexes on the basis of the spectral data. Further, a number of cationic complexes of di- and tri-methyltin tetraphenyl borates with amides have been characterised[2]. However, reports on the acceptor behaviour of triphenyltin pseudohalides towards amides are rare. We report here synthesis and characterisation of the complexes of triphenyltin isocyanate and thiocyanate with dimethylformamide (DMF), diphenylformamide (DPF), dimethylacetamide (DMA), diphenylacetamide (DPA) and dimethyloxamide (DMO).

Triphenyltin isocyanate and triphenyltin isothiocyanate were prepared from triphenyltin halide by a metathetical reaction in acetone solution. For the preparation of adducts the reactants were taken in 1:1 molar ratio and refluxed for 2 hr; the solids obtained were recrystallised from benzene.

The compounds were characterised by their analytical and IR spectral data. Molecular weights were determined cryoscopically in freezing nitrobenzene. The molar conductance values were measured in nitrobenzene at a single dilution of 10^{-4} *M* with Phillips PR-9500 conductivity bridge. The infrared spectra were recorded in KBr on a 621-Perkin Elmer model spectrometer.

The adducts are listed in Table 1. They are colourless, crystalline, thermally stable solids with sharp melting points; the compounds are soluble in common organic solvents.

†Present address: Extractive Metallurgy Division, National Metallurgical Laboratory, Jamshedpur

Table 1—Characterisation Data of the Complexes of Triphenyltin Pseudohalides with Amides

Compound	m.p. (°C)	Mol. wt. Found (Calc.)	Found (Calc.), % Sn	C	H
$Ph_3SnNCO.DMF$	90	325 (465)	24.9 (25.7)	56.0 (56.5)	5.0 (4.7)
$Ph_3SnNCS.DMF$	80	462 (481)	24.7 (24.5)	54.0 (54.8)	4.0 (4.5)
$Ph_3SnNCO.DPF$	81	498 (589)	19.6 (20.0)	63.9 (65.1)	4.6 (4.4)
$Ph_3SnNCS.DPF$	96	587 (605)	23.1 (22.7)	62.8 (63.4)	4.0 (4.3)
$Ph_3SnNCO.DMA$	111	390 (479)	25.0 (24.9)	57.2 (57.6)	4.8 (5.0)
$Ph_3SnNCS.DMA$	113	486 (495)	23.8 (24.0)	53.5 (53.4)	4.4 (4.8)
$Ph_3SnNCO.DPA$	78	489 (603)	19.6 (19.7)	64.8 (65.4)	4.4 (4.6)
$Ph_3SnNCS.DPA$	140	526 (619)	20.0 (19.2)	63.8 (63.9)	4.7 (4.5)
$Ph_3SnNCO.DMO$	169	425 (508)	23.4 (23.4)	55.4 (54.3)	4.0 (4.5)
$Ph_3SnNCS.DMO$	152	431 (524)	23.4 (22.7)	51.3 (52.7)	4.0 (4.3)

The molecular weights of the complexes determined in nitrobenzene establish their monomeric nature; somewhat low observed values may be attributed to the slight dissociation on dissolution in the solvent (Table 1). The molar conductances of the compounds in nitrobenzene falling in the range 2.6-6.6 ohm^{-1} cm^2 mol^{-1} indicate their non-electrolytic nature.

A comparison of infrared spectra (in cm^{-1}) of the ligands with those of their complexes reveals the bonding mode of the amides to the lewis acids. In DMF, the $\nu C=O$ mode appears at 1666, but it shifts to 1650 and 1631 in the spectra of complexes with Ph_3SnNCO and Ph_3SnNCS, respectively. The $\nu C=O$ mode of free DPF identified at 1685 undergoes a negative shift of 30 and 35 for the cyanate and thiocyanate adducts respectively. These observations are in conformity with the earlier reports[3-5], thus suggesting the bonding of the ligands through the oxygen atom. For the DMA and DPA derivatives, $\nu(C=O)$ mode showed a negative shift of 21-23 and 68-70 respectively. The bonding through both of the O-atoms of the DMO is indicated as the $\nu C=O$ of the free ligand, present at 1685, appears around 1660 in its complexes. The νN-H mode of the DMO does not show any significant change indicating absence of coordination through the nitrogen.

A positive shift of 10-35 in the νC-N (contiguous to the νC=O group), located at 1243-1320 in the free ligands[6], on complexation, is attributed to the O-bonding of the amides. Complexation through oxygen is further substantiated[7] by the appearance of νSn-O in the range 405-367.

The ν_{as}(CN) mode for Ph_3SnNCO and Ph_3SnNCS is found at 2230 and 2083 respectively; it undergoes negative shift of about 30 in the spectra of adducts. This indicates an increase in the coordination number around tin atom[8] and the absence of bridging NCO or NCS groups. Thus, the adducts studied here are five-coordinated except the DMO derivatives which are six coordinated.

The antibacterial activities of the lewis acids and their adducts were tested against *B. subtilis* and *S. aureus*. The ethanolic solutions of the compounds were used in the two-fold serial dilution method[9] and the data for MIC (minimum inhibitory concentration) were collected. The antifungal activities of the compounds were also examined against four types of fungi. The results indicate that the biocidal properties of the compounds are significantly improved in most cases as a consequence of the complexation.

The authors thank Prof. T N Srivastava, Chemistry Department, Lucknow University, Lucknow for helpful suggestions and discussion.

References

1 Drago R S & Matwiyoff N A, *Inorg Chem*, **3** (1964) 337.
2 Dass V G K & Mitching W, *J organometal Chem*, **10** (1967) 59.
3 Archambault J & Rivest R, *Can J Chem*, **38** (1960) 1331.
4 Paul R C, Singh P, Makhni H S & Chadha S L, *J inorg nucl Chem*, **32** (1970) 3964; *Z anorg allg Chem*, **377** (1970) 108.
5 Matsubayashi G, Tanaka T & Okawara R, *Bull chem Soc Japan*, **30** (1968) 1831.
6 Bellamy L J, *The infrared spectra of complex molecules* (John Wiley, New York) 1958, 231.
7 Nakamoto K, *Infrared and Raman spectra of inorganic and coordination compounds* (John Wiley, New York) 1978, 235.
8 Holloway J H, Mc Quillan G P & Ross D S, *J chem Soc*, A (1969) 2505.
9 Srivastava T N & Rupainwar R, *Indian J Chem*, **9** (1971) 1411.