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Thermal properties of some di(4-substituted phenyl)tin dichloride complexes with nitrogen donor ligands

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The thermal properties of some organotin complexes of general structure $(4\text{-}ZC_6H_4)_2SnCl_2.L_2$ (Z=Me, CF_3, F, Cl, OMe and H; L_2 = 2,2′-bipyridyl and 4,4′-dimethyl-2,2′-bipyridyl) are reported. The thermal data obtained by Differential Thermal Analysis (DTA) for these complexes is reported. Thermal decomposition experiments for some of the complexes are described and indicate a disproportionation of the complexes into the aryltin trichloride complex and the triaryltin chloride. The controlled decomposition provides a possible alternative preparative route to some aryltin trichloride complexes.

Keywords: Organotin complexes, aryltin chlorides, differential thermal analysis

INTRODUCTION

Anti-tumour activity has been demonstrated for many diorganotin(IV) dihalide complexes, which are analogues of the drug, Cisplatin. In this journal,[1] we have reported the synthesis and some spectroscopic properties of a series of octahedral di(4-substituted phenyl)tin dichloride complexes prepared as part of a programme of structure–activity relationship studies. During melting-point determination it was noted that some of the bipyridyl complexes showed unusual behaviour.[1,2] These observations have led us to examine the thermal stability of these complexes in more detail and the work is described here. We have found no reference to the thermal properties of these or related compounds in the literature.

EXPERIMENTAL

Preparation of diaryltin(IV) dichloride complexes

Methods of preparation and analytical data for the complexes of the diaryltin dichlorides, $(4\text{-}ZC_6H_4)_2SnCl_2.L_2$ where Z = Me, F, CF_3, OMe and Cl and L_2 = 2,2′-bipyridyl, are fully reported in a previous paper.[1] The parent complex where Z = H and L_2 = 2,2′-bipyridyl is also well characterized.[3]

The complexes where Z = Me and F and L_2 = 4,4′-dimethyl-2,2′-bipyridyl (Me_2bipy) were obtained by adding a solution of the diaryltin dichloride (0.01 mol) in methanol (5 cm^3) to a solution of the Lewis base (0.01 mol) in methanol (5 cm^3) at room temperature. The complexes, which separated rapidly, were filtered off and dried in air.

(a) $(4\text{-}MeC_6H_4)_2SnCl_2.Me_2$bipy (yield 90%), m.p.207–208°C (232–234°C)[4] (Found: C,56.25; H,4.68; Cl,12.68; N,4.93. $C_{26}H_{26}Cl_2N_2Sn$ requires C,56.15; H,4.71; Cl,12.75; N,5.04%).

(b) $(4\text{-}FC_6H_4)_2SnCl_2.Me_2$bipy (yield 90%), m.p.221–222°C dec. (Found: C,50.70; H,3.65; N,5.10. $C_{24}H_{20}F_2Cl_2N_2Sn$ requires C,51.11; H,3.57; N,4.97%). This complex is hitherto unreported in the literature.

Preparation of triaryltin(IV) chlorides

(a) Tris(4-methylphenyl)tin chloride

Tetrakis(4-methylphenyl)tin (0.2 g, 4.41 × 10^{-4} mol) and bis(4-methylphenyl)tin dichloride (0.164 g, 4.41 × 10^{-4} mol) were heated together at an oil-bath temperature of 180°C for 2 h. Extraction of the solid product with 40–60°C petroleum spirit yielded

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0.183 g (52%) of material, m.p. 83–85°C. Two further crystallizations from the same solvent yielded pure material, m.p. 88.5–89°C (lit.95.5°C)[5] (Found: C,58.43; H,4.91; Cl,8.25. $C_{21}H_{21}ClSn$ requires C,58.99; H,4.95; Cl,8.29%).

(b) Tris(4-fluorophenyl)tin chloride

Tetrakis(4-fluorophenyl)tin (1.0 g, 2.0×10^{-3} mol) and bis(4-fluorophenyl)tin dichloride (0.8 g, 2.1×10^{-3} mol) were heated together at an oil-bath temperature of 170–180°C for 3 h. Extraction of the cooled product with 40–60°C petroleum spirit yielded the solid product (0.870 g, 48%), m.p.84–86°C. Three further crystallizations gave pure material, m.p.102–103°C (lit.118–120°C)[6] (Found: C,49.15; H,2.75. $C_{18}H_{12}F_3ClSn$ requires C,49.20; H,2.75%).

Preparation of aryltin(IV) trichloride 2,2′-bipyridyl complexes

(a) 4-Methylphenyltin trichloride. 2,2′-bipyridyl(1:1)

Tetrakis(4-methylphenyl)tin (0.3 g, 6.21×10^{-4} mol) and tin tetrachloride (0.5 g, 1.86×10^{-3} mol) were dissolved in toluene (2 cm^3) and heated under reflux for 6 h. The resulting solution was diluted with toluene and filtered into a toluene solution of 2,2′-bipyridyl (0.39 g, 2.48×10^{-3} mol) to give an immediate precipitate of the complex (1.0 g, 84%), m.p. 265–267°C (Found: C,43.08; H,3.18; Cl,22.78; N,5.87. $C_{17}H_{15}Cl_3N_2Sn$ requires C,43.17; H,3.17; Cl,22.54; N,5.93%).

(b) 4-Fluorophenyltin trichloride. 2,2′-bipyridyl (1:1)

Tetrakis(4-fluorophenyl)tin (0.50 g, 1.00×10^{-3} mol) and tin tetrachloride (0.78 g, 3.00×10^{-3} mol) were dissolved in toluene (1 cm^3) and heated under reflux for 4 h, diluted with toluene and filtered into a solution of 2,2′-bipyridyl (0.63 g, 4.00×10^{-3} mol). The precipitate was filtered off, washed with methanol and air dried to give the product (1.50 g, 79%), m.p. 261–264°C. Recrystallization from ethanol gave the complex, m.p. 261–262°C (Found: C,40.79; H,3.00; Cl,21.85; N,5.54. $C_{16}H_{12}FCl_3N_2Sn$ requires C,40.34; H,2.54; Cl,22.33; N,5.88%).

(c) 4-Methoxyphenyltin trichloride. 2,2′-bipyridyl(1:1)

The preparation was carried out as described in (b) above. The complex separated as a colourless solid (yield 82%), m.p. 239–241°C (Found: C,41.17; H,2.94; Cl,22.40; N,5.77. $C_{17}H_{15}Cl_3N_2OSn$ requires C,41.80; H,3.09; Cl,21.78; N,5.74%). These complexes are hitherto unreported in the literature.

Thermal decomposition experiments

(a) Decomposition of bis(4-methylphenyl)tin dichloride. 2,2′-bipyridyl (1:1)

Bis(4-methylphenyl)tin dichloride.2,2′-bipyridyl (1:1) (0.3 g, 5.68×10^{-4} mol) in a small hard glass tube, fitted with a cold-finger condenser, was heated in an oil bath at a temperature of 225–230°C for 5 min. The reaction vessel was cooled. The crystalline sublimate on the cold finger was removed and was identified as 2,2′-bipyridyl by melting point (m.p.) determination and by infrared (IR) spectroscopy by comparison with an authentic sample. The reaction vessel was reweighed and the loss in weight, representing the loss in 2,2′-bipyridyl from the tube, (0.04 g, 2.56×10^{-4} mol) was noted.

The solid mass remaining in the reaction tube was extracted with several portions of cold methanol. The combined methanol extracts were evaporated to yield impure tris(4-methylphenyl)tin chloride (0.105 g, 2.46×10^{-4} mol). Crystallization from 40–60°C petroleum spirit yielded pure material, m.p. 88–89°C, identical with an authentic sample prepared as described above. The m.p. values and IR spectra were identical.

The remaining insoluble material was shown by analysis and comparison with an authentic sample, prepared as described above, to be 4-methylphenyltin trichloride.2,2′-bipyridyl (1:1) (0.117 g, 2.48×10^{-4} mol), m.p. 265–267°C (Found: C,43.24; H,3.14; Cl,22.03; N,5.84. $C_{17}H_{15}Cl_3N_2Sn$ requires C,43.17; H,3.17; Cl,22.54; N,5.93%).

(b) Decomposition of bis(4-fluorophenyl)tin dichloride.2,2′-bipyridyl (1:1)

Bis(4-fluorophenyl)tin dichloride.2,2′-bipyridyl (0.500 g, 1×10^{-3} mol) was heated as described in (a) above at a temperature of 230–235°C for 5 min. A crystalline sublimate on the cold finger was shown to be 2,2′-bipyridyl only by m.p., mixed m.p. and IR spectroscopy on comparison with a sample of 2,2′-bipyridyl (recrystallized laboratory reagent). The reaction vessel was reweighed and the loss in weight due to 2,2′-bipyridyl (0.064 g, 4.1 × 10^{-4} mol) was noted.

The solid mass remaining in the reaction tube was extracted with several portions of boiling hexane. The combined hexane extract was concentrated to about 2 cm^3 to give a colourless crystalline solid, shown to be tris(4-fluorophenyl)tin chloride, m.p. 102–103°C (Found: C,49.29; H,2.70; Cl,8.18. $C_{18}H_{12}ClF_3Sn$ requires C,49.20; H,2.75; Cl,8.07%). The m.p. and IR spectrum of this material were identical with those of a sample prepared by the synthetic method described above. The weight of the tris(4-fluorophenyl)tin chloride extracted from the reaction products was recorded as a loss in weight (0.202 g, 4.6 × 10^{-4} mol).

The insoluble material remaining in the tube was shown by elemental analysis and comparison with an authentic sample, prepared as described above, to be 4-fluorophenyltin trichloride.2,2′-bipyridyl (1:1) (0.234 g, 4.9 × 10^{-4} mol), m.p. 264°C (Found: C,40.05; H,2.60; Cl,22.55; N,5.81. $C_{16}H_{12}FCl_3Sn$ requires C,40.34; H,2.54; Sl,22.33; N,5.88%).

(c) Action of heat on bis(4-methoxyphenyl)tin dichloride. 2,2′-bipyridyl (1:1)

Bis(4-methoxyphenyl)tin dichloride. 2,2′-bipyridyl (0.2 g, 3.67 × 10^{-4} mol) was heated above its melting point at 205–210°C for 15 min. as described in experiments (a) and (b). During this time a small amount of 2,2′-bipyridyl collected on the cold-finger condenser. The molten residue was cooled, washed with a little cold methanol and shown to be unchanged starting complex (0.172 g, 86% recovery), m.p. 192–194°C. The IR spectrum of this material was identical with that of starting material and different in several regions from the spectrum of 4-methoxyphenyltin trichloride. 2,2′-bipyridyl prepared as described above.

Differential thermal analysis

Differential thermal analysis (DTA) traces were run at 4 K min^{-1} on a Stanton Redcroft Differential Thermal Analyser Model 671. All samples were run in static air and from ambient temperature to 320°C. The reference substance was alumina (analytical reagent quality).

RESULTS AND DISCUSSION

Observations made during melting point determination on many diaryltin(IV) complexes indicate extensive decomposition. A sublimate is often noted in the capillary tube and only partial melting occurs. If heating is continued, solid material often remains until a temperature at least 30°C above the initial decomposition is achieved.

In order to gain further information on the processes occurring, a series of eight diaryltin dichloride complexes, all previously reported except compound (h),[1] was subjected to differential thermal analysis. These results are shown in Fig. 1 below.

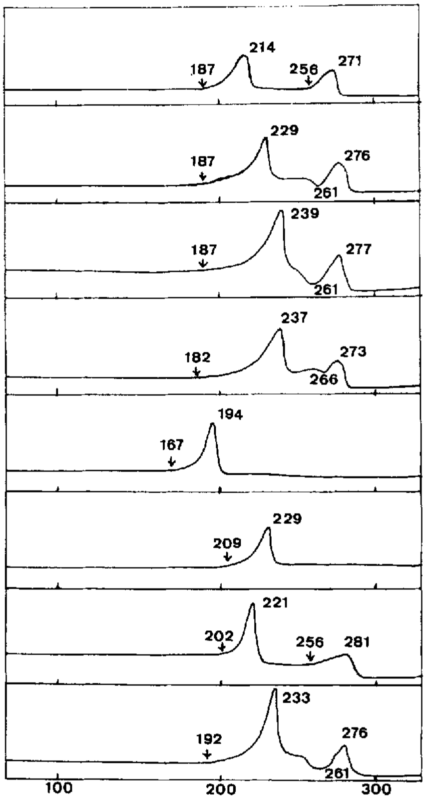

Figure 1 Thermograms of some di-(4-substituted phenyl)tin(IV) dichloride complexes, $(ZC_6H_4)_2SnCl_2.L_2$. Complexes where L_2 = 2,2′-bipyridyl: (a) Z = Me, (b) Z = F, (c) Z = CF_3, (d) Z = H, (e) Z = OMe and (f) Z = Cl. Complexes where L_2 = 4,4′-dimethyl-2,2′-bipyridyl: (g) Z = Me and (h) Z = F.

For each of the complexes, a low-temperature endothermic process occurs, which corresponds well with the observed published melting-point values. The broad temperature range observed in each case probably indicates, however, a decomposition or dissociation process taking place. In all cases, except the 4-chloro and 4-methoxy derivatives, a second higher-temperature endothermic process is seen to occur, corresponding to melting or decomposition of a product of the initial low-temperature process.

Product analysis studies on the thermal decomposition of two of the complexes (Z = Me and F) which show a high-temperature endothermic change were carried out. These complexes, on heating for a short time at the lower temperature indicated by the DTA trace, readily lost some of the bidentate ligand (2,2′-bipyridyl) to leave a residue from which were isolated in each case the triaryltin chloride, $(ZC_6H_4)_3SnCl$, and the 2,2′-bipyridyl complex of the aryltin trichloride, $ZC_6H_4SnCl_3$. The volatility of the chelating bipyridyl molecule, together with the large solubility difference between the monochloride and the trichloride complex, enabled the stoichiometry of the thermal decomposition to be established. This is expressed in Eqn [1]:

$$2\ (ZC_6H_4)_2SnCl_2.bipy \rightarrow (ZC_6H_4)_3SnCl + ZC_6H_4SnCl_3.bipy + bipy \qquad [1]$$

A similar experiment was carried out with the 4-methoxy derivative but, in this case, conversion to the aryltin trichloride complex did not occur. This observation agrees with the absence of a high-temperature transition in the thermal analysis trace. Slow decomposition of the complex was found to occur, however, to give a small amount of the free chelating agent. Most of the diaryltin dichloride complex was recovered unchanged.

Although conversion to the aryltin trichloride complex does not occur in the case of the 4-methoxy and 4-chloro compounds by the thermal decomposition process described above, no difficulty was encountered in preparing samples of the two complexes by standard Kocheshkov comproportionation procedures, followed by reaction with the chelating agent (Eqns [2] and [3]):

$$Ar_4Sn + 3\ SnCl_4 \rightarrow 4\ ArSnCl_3 \xrightarrow{L_2} 4\ ArSnCl_3.L_2 \qquad [2]$$

$$Ar_2SnCl_2 + SnCl_4 \rightarrow 2\ ArSnCl_3 \xrightarrow{L_2} 2\ ArSnCl_3.L_2 \qquad [3]$$

The preparation of a series of new complexes using the procedures described in Eqns [2] and [3] where Z = Me, F and Me has been described in the Experimental section. Differential thermal analysis for these complexes shows that they are stable with melting point–decomposition temperatures higher than 240°C.

All the above experimental observations are consistent with the general reaction scheme for the thermal decomposition shown below (Eqns [4]–[6]).

$$Ar_2SnCl_2.L_2 \rightarrow Ar_2SnCl_2 + L_2 \qquad [4]$$

$$2Ar_2SnCl_2 \rightarrow ArSnCl_3 + Ar_3SnCl \qquad [5]$$

$$ArSnCl_3 + L_2 \rightarrow ArSnCl_3.L_2 \qquad [6]$$

Step [4] is observed to occur for all complexes and, in the case of the 4-chloro compound, a small amount of the free di(4-chlorophenyl)tin dichloride has been isolated and characterized. For most complexes we presume that a thermal disproportionation step [5] then leads to the solid $ArSnCl_3.L_2$ via step [6]. Decreasing the number of chlorine atoms joined to tin in the general complex, $Ar_nSnCl_{(4-n)}$ is known to decrease complex stability. The complexes of Ar_3SnCl ($n=3$) are unstable and octahedral complexes with bidentate ligands are unknown. This accounts for the isolation of uncomplexed triaryltin chloride formed in step [5]. The volatility of the free bipyridyl and the high stability of the monoaryl trichloride complex accounts for the high yields (near quantitative) of the products and thereby suggests preparative possibilities. In the case of the 4-methoxy and 4-chloro compounds, however, no conversion to the trichloride complex occurs, although these complexes have been prepared and have high stability. This implies a high stability for the dichloride complexes, where Z = OMe and Cl, preventing any significant dissociation. It is difficult to reconcile this with the substituent parameters for methoxy and chloro and the other substituents in the series, although normal polar influences may not be operating in this high-temperature thermal decomposition.

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