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Coordination Chemistry of Organometallic Bases of Group IV Elements. Part IV[†]: 2:1 Adducts of Antimony(V) Chloride and μ-Oxo-bis[triorganotin(IV)] Compounds.

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Two mol of antimony(V) chloride and one mol of μ-oxo-bis[tri-n-propyl/tri-n-butyl or triphenyl tin(IV)] compound (L) react in carbon tetrachloride and/or dichloromethane at ice water temperature to give solid compounds of composition $L\cdot 2SbCl_5$. Elemental analyses, molar conductances, infrared spectral data, as well as metathetical reactions with silver nitrate and silver perchlorate in acetonitrile solution, point to the ionic structure $[(R_3Sn)_2O: \rightarrow SbCl_4]^+[SbCl_6]^-$ of these adducts.

Introduction

Oxo-organotin compounds are basic in nature [1] and are known to give addition compounds of 1:1 and 1:2 (acid:base) stoichiometry with common Lewis acids [2, 3]. μ-Oxo-bis[triorganotin(IV)] compounds react with nickel(II), cobalt(II) and iron(III) chlorides in appropriate solvents to give new types of coordination complexes [4, 5]. These bases also react with liquid sulphur trioxide to give addition compounds which later change to organotin sulphates and disulphates [6]. However, there is no report about the reactions of excess of antimony(V) chloride towards these bases. The reactions of twofold excess of antimony(V) chloride with μ-oxo-bis[tri-n-propyl/tri-n-butyl and triphenyl tin(IV)] compounds were therefore studied.

Experimental

μ-Oxo-bis[tri-n-propyl, tri-n-butyl and triphenyl tin(IV)] compounds (Akzo Chemicals Ltd. Kirby, U.K.) were used as obtained. Antimony(V) chloride (Reidel pure) was distilled before use. Silver nitrate (AR grade) and silver perchlorate (Fluka A.G.) were used as received. Acetonitrile (BDH Pure) was purified as reported [7].

Physical Measurements

Infrared spectra of the complexes were recorded on Perkin-Elmer (Models 337 and 621) spectrophotometers. These instruments are occasionally calibrated with standard polystyrene film. The spectra were taken as Nujol mulls, fluorolube mull or as potassium bromide pellets.

Resistances of the complexes in dry acetonitrile were measured on conductolyser (model 5300 B, LKB Produkter AB Sweden) in the range 0–10,000 ohms. The higher values were determined by employing shunts of known resistances [8]. The cell constant (0.2185 ± 0.0002) of a dip-type cell was determined by the standard method [9].

Preparation of Complexes

Antimony(V) chloride in dry carbon tetrachloride was added dropwise to μ-oxo-bis[tri-n-propyl/tri-n-butyl or triphenyl tin(IV)] in the molar ratio 2:1 (acid:base) in the same solvent or dry dichloromethane under a current of dry nitrogen over a period of 1/2 h. The reaction mixtures were magnetically stirred and kept in an ice-water bath (0–5 °C) during the reaction. After about 2 h the complexes were filtered cold under a slow bubbling current of dry nitrogen, washed with the solvents, dried in a vacuum, and analysed. The elemental analyses were carried out at UMIST, Manchester, England.

Metathetical Reactions

Silver nitrate or silver perchlorate in acetonitrile was added dropwise into the solution of a complex in the same solvent in equimolar quantities in the atmosphere of dry nitrogen. A white solid, sensitive to light, was precipitated in each case and was isolated. The compound analysed as $AgSbCl_6$.

The removal of solvent from the filtrates in vacuum gave light-yellow compounds. The analytical data are presented in Table I.

Results and Discussion

The adducts are moisture-sensitive, infusible solids which deteriorate on heating (100 °C) and which

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TABLE I. Analytical Data of 2:1 Adducts of Antimony(V) Chloride with μ-Oxo-bis[triorganotin(IV)] Compounds as well as of the Products of Metathetical Reactions.

Compounds		Analysis Found (Calc) %					
		Sb	Sn*	Cl	C	H	N
1	$[L \rightarrow SbCl_4]^+[SbCl_6]^-$	21.5 (21.9)	21.1 (21.3)	31.8 (31.9)	19.4 (19.4)	3.7 (3.8)	–
2	$[L' \rightarrow SbCl_4]^+[SbCl_6]^-$	20.1 (20.4)	19.8 (19.9)	29.5 (29.7)	24.8 (24.0)	4.4 (4.5)	–
3	$[L'' \rightarrow SbCl_4]^+[SbCl_6]^-$	18.2 (18.5)	18.2 (18.0)	26.8 (27.0)	32.6 (32.8)	2.0 (2.2)	–
4	$[L \rightarrow SbCl_4]^+[NO_3]^-$	14.3 (14.5)	28.4 (28.6)	16.7 (16.9)	25.1 (25.7)	4.8 (5.0)	1.5 (1.6)
5	$[L' \rightarrow SbCl_4]^+[NO_3]^-$	13.1 (13.2)	25.7 (25.8)	15.2 (15.4)	31.0 (31.2)	5.5 (5.8)	1.3 (1.5)
6	$[L'' \rightarrow SbCl_4]^+[NO_3]^-$	11.4 (11.7)	23.0 (23.1)	13.4 (13.6)	41.2 (41.4)	2.6 (2.8)	1.0 (1.3)
7	$[L \rightarrow SbCl_4]^+[ClO_4]^-$	17.1 (17.3)	27.0 (27.3)	25.4 (25.2)	30.5 (30.7)	5.5 (5.6)	–
8	$[L' \rightarrow SbCl_4]^+[ClO_4]^-$	12.3 (12.4)	25.0 (24.8)	18.5 (18.4)	29.8 (29.9)	5.4 (5.6)	–
9	$[L'' \rightarrow SbCl_4]^+[ClO_4]^-$	11.2 (11.4)	22.1 (22.4)	16.2 (16.4)	42.5 (42.8)	2.6 (2.7)	–

L = μ-oxo-bis[tri-n-propyltin(IV)]. L′ = μ-oxo-bis[tri-n-butyltin(IV)]. L″ = μ-oxo-bis[triphenyltin(IV)]. *Sn was estimated from mixed oxides.

could not be sublimed even under vacuum (10^{-2} mm). These compounds are insoluble in most of the common organic solvents, except in pure acetonitrile where they have limited solubility. Conductances in the concentration range 5×10^{-4} to 57×10^{-4} mol $litre^{-1}$ in this solvent are in the range 70–80 ohm^{-1} cm^2 mol^{-1} [10]*. All attempts to crystallise the compounds failed.

The infrared spectra of pure μ-oxo-bis[tri-n-propyl/tri-n-butyl and triphenyl tin(IV)] show sharp bands between 768–784 cm^{-1} [12–14], which is diagnostic of the presence of a SnOSn bond in the molecules. On adduct formation (Table II) these bands shift lower by 48–67 cm^{-1}. New bands between 435–450 cm^{-1} may be attributed to the formation of $O{:}\rightarrow Sb$ bonds in the adducts [15]. These observations indicate that oxygen is the donor site in these ligands. A group of absorptions between 350–275 cm^{-1} indicate the presence of SbCl bonds in the complexes. However, a comparison of these absorptions with those known for 1:1 adducts of these bases [2], as well as for other oxy bases with antimony(V) chloride, may suggest the ionic nature of these adducts [16, 17] (see also molar conductances, Table III).

The ionic nature of these complexes has been confirmed by metathetical reactions of the adducts with silver nitrate or silver perchlorate in acetonitrile. Whereas the solid obtained from the reactions is $AgSbCl_6$ in each case, the complexes isolated after removal of the solvent, as evidenced by elemental analyses and infrared spectral data (Table I, II) and (Fig. 1) are: $[(R_3Sn)_2O{:}\rightarrow SbCl_4]^+X^-$.

The reaction can thus be represented as:

$$[(R_3Sn)_2O{:}\rightarrow SbCl_4]^+[SbCl_6]^- + AgX \longrightarrow [(R_3Sn)_2O{:}\rightarrow SbCl_4]^+X^- + AgSbCl_6.$$

(where R = n-Pr, n-Bu or Ph and X = NO_3 or ClO_4).

From the above studies, it may be concluded that the adducts are $[(R_3Sn)_2O{:}\rightarrow SbCl_4]^+[SbCl_6]^-$. The pentacoordinated tetrachloro stibonium(V) cation obtained here was previously unknown.

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*These values are nearly half of those normally required for 1:1 electrolytes. Detailed analyses of equivalent conductance *vs.* concentration data using the Fuoss-Onsager-Skinner and Fernandez–Prini equations [10, 11] and comparison of experimental and theoretical Onsager slopes reveal the adducts to be completely dissociated strong 1:1 electrolytes.

TABLE II. Some Major Infrared Absorptions of 2:1 Adducts of Antimony(V) Chloride with µ-Oxo-bis[tri-n-propyl/tri-n-butyl/triphenyl tin(IV)] Compounds as well as Those of the Metathetical Reaction Products in the Range 1200–200 cm^{-1}.

$[B \rightarrow SbCl_4]^+[SbCl_6]^-$	$[B \rightarrow SbCl_4]^+[NO_3]^-$	$[B \rightarrow SbCl_4]^+[ClO_4]^-$	$AgSbCl_6$	Assignment
280–275			280–275	νSb–Cl
325–315			315–305	(anionic)
345–335	350–335	345–330	–	νSb–Cl
355				(cationic)
446	440	445		$\nu_{as}SnPh_3$
450–435	450–440	450–435	–	$O: \rightarrow Sb$
–	–	460		ClO_4^-
520–515	518	–	–	$\nu_sSn–C_3$
565–560	560–555	565–560	–	$\nu_{as}Sn–C_3$
–	712–710	–	–	NO_3^-
727–717	730–725	725–720	–	$\nu_{as}Sn–O–SN$
–	810–800	–	–	NO_3^-
–	–	928	–	ClO_4^-
–	–	1120	–	ClO_4^-

B = L, L′ or L″ (as in Table I).

TABLE III. Limiting Molar Conductances, Experimental and Theoretical Slopes of the Λ *vs.* $\sqrt{c}$ Plot of 2:1 Adducts of Antimony(V) Chloride with µ-Oxo-bis[tri-n-butyltin(IV)] and µ-Oxo-bis[triphenyltin(IV)].

Compounds	Λ_0* (ohm^{-1} cm^2 mol^{-1})	Onsager slope	Exptl slope	Exptl slope / Theoretical slope
$[L' \rightarrow SbCl_4]^+[SbCl_6]^-$	76.00	289.80	260.00	0.89
$[L'' \rightarrow SbCl_4]^+[SbCl_6]^-$	69.60	285.20	320.00	1.12

*Obtained by extrapolation method.

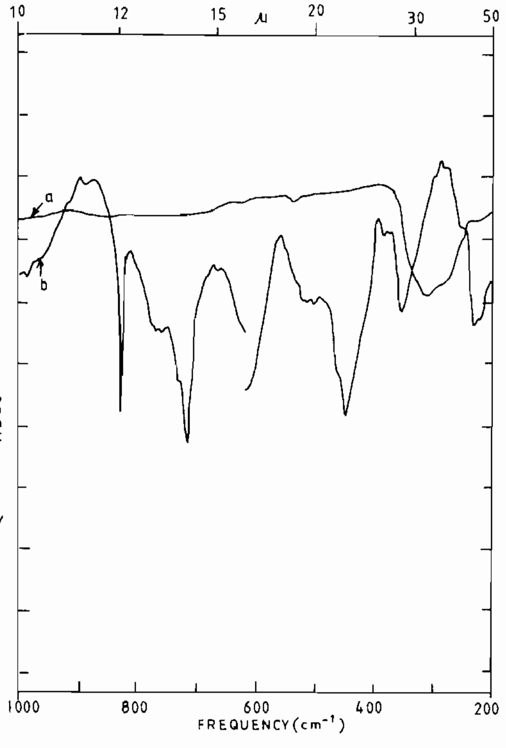

Fig. 1. Infrared spectra of (a) $AgSbCl_6$, (b) $[[(C_4H_9)_3Sn]_2O: \rightarrow SbCl_4]^+[NO_3]^-$.

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