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COMPLEXES OF ORGANOMETALLIC COMPOUNDS

XLIII. SYNTHESIS AND INFRARED SPECTRA OF FLUORO-, CHLORO- AND BROMO-PHENYLANTIMONATES(V)

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Summary

The synthesis of halogenophenylantimonates(V) M^IPhSbX_5 (M^I = Me_4N, Ph_4As; X = F, Cl, Br) is described, and their IR spectra (1100-100 cm^{-1}) interpreted.

Introduction

A study of the formation and structure of organoantimony anionic complexes with halide and pseudohalide ligands was recently initiated in our laboratory, and the first characterization of some diphenylantimonates(V) of the type $M^IPh_2SbCl_3X$ ($M^I = Me_4N$ or Ph_4As; X = Cl, Br, N_3, NCS) reported [1]. The preparations of solid phenylantimonates M^IPhSbX_5 (M^I = Me_4N and Ph_4As; X = F, Cl, Br) are now described.

Although several chloro salts $MArSbCl_5$ (M = NH_4, PyH, ArN_2, etc.; Ar = Ph or substituted phenyl) (see for instance refs. 2-5) and one example of a bromo-derivative, PyH[β-naphtyl-$SbBr_5$] [3], have been known for a long time, this type of compound has been little studied, the corresponding fluoro-derivatives have not been reported. Since the literature contains practically no vibrational data for monoorganoantimony species [6], we measured the infrared spectra of the new compounds, and of $NH_4PhSbCl_5$, in the solid state. The data have been interpreted and principal bands assigned as far as is possible in the light of previously reported IR data for phenylantimony compounds [7-12].

Experimental

Analytical grade reagents were used. The ammonium salt, $NH_4PhSbCl_5$, prepared as described by Schmidt [2], was used as the source of the monophenylantimony moiety.

TABLE 1

MELTING POINTS (°C) AND ANALYTICAL DATA [FOUND (CALCD.) %]

Compound	m.p.	Analysis			
		C	H	N	Halogen
$Me_4NPhSbF_5$	236-239	32.62 (32.63)	4.80 (4.66)	3.91 (3.81)	25.59 (25.81)
$Ph_4AsPhSbF_5$	196-198	52.79 (52.82)	3.83 (3.69)		13.81 (13.93)
$Me_4NPhSbCl_5$	198-200	26.49 (26.67)	3.91 (3.81)	3.13 (3.11)	39.28 (39.37)
$Ph_4AsPhSbCl_5$	208-211	47.18 (47.44)	3.52 (3.32)		23.13 (23.34)
$Me_4NPhSbBr_5$	192-195	[a]	2.90 (2.55)	2.20 (2.08)	59.25 (59.41)
$Ph_4AsPhSbBr_5$	198-200	36.67 (36.70)	3.03 (2.57)		40.85 (40.70)

[a] ~1% error (see text).

Known amounts (~1 g) of $NH_4PhSbCl_5$ were hydrolyzed in water (at pH ~3 with dilute sodium hydroxide) to phenylstibonic acid which was separated by centrifugation and dissolved in the minimum volume (~15 ml) of a mixture aq. conc. HX/EtOH 3/1. The addition of stoichiometric amounts of M^ICl (M^I = Me_4N or Ph_4As) dissolved in the same HX/EtOH solvent mixture caused the precipitation of M^IPhSbX_5. The fluoro and chloro salts were recrystallized from EtOH or MeOH, while the less soluble bromo-derivatives were thoroughly washed with MeOH.

Typical analytical data are given in Table 1. Analyses on various samples of $Me_4NPhSbBr_5$, from different preparations, were not completely satisfactory, and the compound was contaminated by a Sb^{III}-containing species. However, the infrared spectra of the two bromo salts are similar, suggesting that the same organoantimony residue is present in both.

The infrared spectra were recorded in the ranges 4000-250 cm^{-1} and 500-100 cm^{-1} with Perkin—Elmer 457 and Beckman IR 12 spectrometers, respectively. Compounds were examined as Nujol mulls between KBr or polythene plates; the use of CsI plates had to be avoided as they often reacted (iodide oxidation) with the samples. Table 2 lists the infrared data in the 1100-100 cm^{-1} region.

Discussion

Detailed assignments of vibrational bands due to phenyl ring vibrations in phenylantimony derivatives [7-12] have been almost invariably made by reference to Whiffen's assignments [13] for the monosubstituted halobenzenes, and we used the same procedure. Analysis of spectra was restricted to the region below 1100 cm^{-1} (Table 2), where the phenyl modes (X- or mass-sensitive [13]), and the antimony—halogen vibrations occur.

Once counterion absorptions are considered (phenyl mass-insensitive modes of the Ph_4As group cannot be distinguished from the corresponding

TABLE 2

INFRARED SPECTRA OF HALOGENOPHENYLANTIMONATES $\mathrm{M^IPhSbX_5}$

X = F		X = Cl			X = Br		Assignment[a]
$\mathrm{M^I = Me_4N}$	$\mathrm{M^I = Ph_4As}$	$\mathrm{M^I = NH_4}$[b]	$\mathrm{M^I = Me_4N}$	$\mathrm{M^I = Ph_4As}$	$\mathrm{M^I = Me_4N}$	$\mathrm{M^I = Ph_4As}$	
1090ms	1085s	1090vw	1090vw	1085ms	1090vw	1085ms	*d*- and *q*(*x*-sens)-mode
1080(sh)	1075(sh)	1060vw	1065(sh)	1070(sh)	1060vw	1070(sh)	
		1050mw	1055mw	1055w	1045m	1050w	
1030mw	1025mw	1020m	1020m	1025mw	1015mw	1025w	*b*-mode
				1020mw		1015w	
1000m	1000ms	995ms	1000ms	1000ms	990s	1000ms	*p*-mode
	995(sh)			995(sh)		995m	
	985vw			975w	965vw	970vw	*j*- and *h*-mode
	975vw						
955vs			950vs		945vs		$\rho(\mathrm{CH_3})$ of $\mathrm{Me_4N}$
	935vw			935vw		930vw	*i*-mode
	920vw			920vw		920vw	
	850w			845vw		850vw	*g*-mode
	845w			840vw		845vw	
						830vw	
760vs	765ms						ν(SbF)
750vs	750(sh)	730vs	740vs	750(sh)	740vs	750s	*f*-mode
	740vs		725(sh)	740vs	725(sh)	740(sh)	
				725(sh)		735vs	
						725(sh)	
705vs	705ms						ν(SbF)
675vs	670ms	680s	685ms	690s	685ms	690(sh)	*v*- and *r*(*x*-sens)-mode
		660vw	670(sh)	685(sh)	670(sh)	685ms	
				670(sh)		680m	
620vs(br)	615s						ν(SbF)
585vs(br)	590vs						
500w							
	476s			478ms		478ms	*y*(*x*-sens)mode of $\mathrm{Ph_4As}$
	470(sh)			468s		468s	
						465(sh)	
465s	463s	455s	462ms	462s	459s	458ms	*y*(*x*-sens)mode of PhSb
	360(sh)			366ms		365ms	*t*(*x*-sens)mode of $\mathrm{Ph_4As}$
	354s			354ms		353ms	
				346mw		346m	
308vs	300vs						δ(SbF)
300vs							
		320vs(br)	332(sh)	332(sh)			ν(SbCl)
		290(sh)	308vs	315vs			
			288(sh)	305(sh)			
				285(sh)			
273(sh)	275(sh)	275(sh)	270(sh)	268mw	288ms(br)	282mw	*t*(*x*-sens)mode of PhSb?
					262ms	250ms	ν(SbBr)
239s	250m		246ms	246m	244s	244s	*u*(*x*-sens) mode?
	240m						
					226s	223s	ν(SbBr)
					208s	210s	
					190s	194m	
190m	190mw		232(sh)	238w	178(sh)	178w	skeletal deformations
175w	178mw		217ms	217m	158m	160mw	
			177s	177ms	125ms	126m	
			138mw	140w	116(sh)	118(sh)	
				134w			

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[a] Whiffen's nomenclature [13] is used to indicate phenyl vibrations arising from $\mathrm{Ph_4As}$ and PhSb unities.

[b] Spectrum recorded to 250 $\mathrm{cm^{-1}}$.

vibrations of PhSb unity) no difficulty is encountered in assigning all phenyl frequencies down to 350 cm^{-1}. This procedure accounts for all bands observed in the 1100-350 cm^{-1} region of spectra of chloro and bromo salts, but discloses four unassigned features in the range 760-580 cm^{-1} in the spectra of the fluorosalts. These bands may be assigned to antimony—fluorine stretchings in virtue of similar ν(SbF) frequencies reported for Me_2SbF_3 (720, 588, 550 cm^{-1}) [14] and of their average values close to the frequency ν_3 for the octahedral SbF_6^- anion (669 cm^{-1} [15]; 689, 661, 649 cm^{-1} [16]). By analogy with ν_4 for SbF_6^- (350 cm^{-1}) [15,16], a strong absorption around 300 cm^{-1} (split into two components in the tetramethylammonium salt) is attributed to δ(SbF).

Assuming the probable existence in our compounds of octahedral $PhSbX_5^-$ species eight infrared-active fundamentals are expected for the skeleton of C_{4v} symmetry: three SbX stretchings ($2a_1 + e$), one SbC stretching (a_1) and four deformations ($a_1 + 3e$). However, the appearance of four bands attributable to ν(SbX) in $PhSbF_5^-$ (and possibly, in the corresponding chloro and bromo species) indicates that lower symmetries, at least as low as those taking in account the phenyl group orientation, must be considered. Because of this and the complexity of the spectra of chloro and bromo salts, an analysis of the region below 350 cm^{-1} is difficult.

Three additional phenyl vibrations of the PhSb moiety, namely the *t*-, *u*- and *x*-(mass-sensitive)modes, are expected in this range [7-12]. Two of these, the *t*- and *u*-type vibrations, essentially corresponding to the skeletal antimony—phenyl stretching and bending modes [6-8,11,12], are tentatively assigned to bands at about 270 and 240 cm^{-1} because of their appearance in all the spectra. The assignments of ν(SbX) (X = Cl, Br) reported in Table 2 then follow. These latter are consistent with similar frequencies assigned to antimony—halogen stretchings for Me_2SbCl_3 (328 cm^{-1} [14]; 342 cm^{-1} [17]), $MeSbCl_3$ oxinate (315 cm^{-1}) [18], $PhSbCl_3$acac (332 cm^{-1}) [19], $SbCl_6^-$ (ν_3, 348 cm^{-1}) [20] and $SbBr_6^-$ (ν_3, 240 cm^{-1}) [21]. The phenyl *x*-vibration may perhaps coincide with absorptions at about 180 cm^{-1}, but this mode is generally reported as weak in the infrared spectra [8-13]. Consequently, these absorptions as well as the remaining low-frequency bands seem better assigned to skeletal deformations of $PhSbX_5^-$ species.

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