Journal of Organometallic Chemistry, 110 (1976) 175—182
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SYNTHESIS AND LOW-FREQUENCY VIBRATIONAL SPECTRA OF SOME HALO- AND PSEUDOHALO-DIPHENYLANTIMONATES(V)

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(Received October 13th, 1975)

Summary

The syntheses of diphenylantimonates(V) of the type M(I)[Ph_2SbX_4] (M(I) = Ph_4As; X = F, Cl, Br, N_3, NCS; X_4 = Cl_3Br, Cl_3N_3) are described. Far-IR spectra of these compounds and of previously synthesized M(I)[Ph_2SbCl_3X] species (M(I) = Me_4N; X = Cl, Br, N_3; M(I) = Ph_4As; X = NCS) are reported. Raman spectra of tetrafluoro and tetrachloro salts are also given. Vibrational data are interpreted in terms of the presence in the solids of *trans*-$Ph_2SbX_4^-$ species and assignments of skeletal modes are suggested.

So far, little attention has been paid to the formation of halogeno- and pseudohalogeno-diorganoantimonate(V) anions and to the isolation of the corresponding salts. Chloro-derivatives of general formula M(I)[R_2SbCl_4] (M(I) is a monovalent cation) appear to have been the only known examples of this class of compounds until very recently [1—5].

The preliminary report [6] on the preparation of M(I)[Ph_2SbCl_3X] (M(I) = Me_4N; X = Cl, Br, N_3; M(I) = Ph_4As, X = NCS) demonstrated the ability of the diphenylantimony(V) moiety to form hexacoordinated anionic species in the presence of halide or pseudohalide ligands. The present paper shows that a large number of such products can be easily prepared and reports the characterisation of the compounds $Ph_4As[Ph_2SbX_4]$ (X = F, Br, N_3 or NCS) as well as of the tetraphenylarsonium salt of the already reported $Ph_2SbCl_3X^-$ species. The azido- and thiocyanato derivatives are of particular interest since the corresponding R_2SbX_3 compounds are not known.

Several workers have investigated phenylantimony derivatives using vibrational spectroscopy. Far-IR spectra and sometimes Raman spectra, together with the suggested assignments, are available [7—12] for a number of compounds containing $Ph_nSb(V)$ moieties (n = 1,3—6). However no studies of this type appear to have been reported for diphenylantimony(V) derivatives.

TABLE 1

MELTING POINTS, ANALYTICAL DATA, AND MOLAR CONDUCTIVITIES IN ACETONE SOLUTION AT 30°C

Compound		M.p. (°C)	Analysis found (calcd.) (%)				Concn. (mM)	λ_M (ohm^{-1} cm^2 mol^{-1})
			C	H	N	Halogen		
$Ph_4As[Ph_2SbF_4]$	(I)	300—302	58.37	4.23		10.23	4.96	90
			(58.80)	(4.10)		(10.34)	2.94	103
$Ph_4As[Ph_2SbCl_4]$	(II)	292—294	53.72	3.85		17.81		
			(53.97)	(3.85)		(17.70)		
$Ph_4As[Ph_2SbBr_4]$	(III)	261—262	44.42	3.03		32.82		
			(44.17)	(3.09)		(32.65)		
$Ph_4As[Ph_2Sb(N_3)_4]$	(IV)	161—164	52.24	3.74	20.35		4.90	101
			(52.26)	(3.65)	(20.32)		2.50	119
$Ph_4As[Ph_2Sb(NCS)_4]$ [a]	(V)	192—193	54.10	3.56	6.25		4.90	102
			(53.88)	(3.39)	(6.28)		2.50	114
$Ph_4As[Ph_2SbCl_3Br]$	(VI)	276—277	50.23	3.73		4.87 [b]		
			(50.13)	(3.58)		(4.73)		
$Ph_4As[Ph_2SbCl_3N_3]$	(VII)	280—282	53.33	3.81	5.24	13.29		
			(53.53)	(3.74)	(5.20)	(13.17)		

[a] S found: 14.22, Calcd.: 14.39%. [b] Total halide (meq./g).

Experimental

Analytical grade reagents were used throughout. Solvents were employed without further purification or drying. Diphenylantimony trichloride hydrate was obtained by reacting Ph_4Pb (a gift from D.A.P., Marienberg) with $SbCl_3$, and oxidising the product, Ph_2SbCl, with SO_2Cl_2 [13].

Syntheses of the complex salts

The compounds $M(I)[Ph_2SbCl_3X]$ ($M(I) = Me_4N$; X = Cl, Br, N_3; $M(I) = Ph_4As$; X = NCS) were obtained, as previously reported [6], from $Ph_2SbCl_3 \cdot H_2O$ and M(I)X. The corresponding tetraphenylarsonium salts, $Ph_4As[Ph_2SbCl_3X]$ (X = Cl, Br, N_3), were prepared in an analogous way by reacting the starting materials in MeOH, and were recrystallized from MeCN.

The diphenylantimonates $Ph_4As[Ph_2SbX_4]$ (X = F, Br) were prepared by dissolving 2.5 mmol of $Ph_2SbCl_3 \cdot H_2O$ in 30 ml of 1 : 1 HX conc. aq./MeOH mixture and then adding the stoichiometric amount of Ph_4AsCl dissolved in 15 ml of MeOH. The bromo salt, which precipitated immediately, was recrystallized from $MeNO_2$. The fluoro salt crystallized from the reaction mixture only after it had been concentrated and cooled, and it was then recrystallized from 1 : 1 Et_2O/MeOH.

The pseudohalogenoderivatives $Ph_4As[Ph_2SbX_4]$ (X = N_3, NCS) were prepared by refluxing 2.5 mmol of $Ph_2SbCl_3 \cdot H_2O$ with the stoichiometric amount of Ph_4AsCl and a ten-fold excess of NaN_3 or KNCS in 35 ml of MeOH or 130 ml of Me_2CO, respectively, for a few minutes. After filtering off the warm solution, the compounds precipitated on cooling. They were recrystallized from MeOH.

Measurements

Microanalyses were performed by the Laboratorio di Microanalisi, Istituto di Chimica Farmaceutica, University of Padua (Italy). Conductivity measurements were made using a LKB model 5300 B conductivity bridge.

IR spectra were recorded for solid samples in Nujol mulls in the regions 4000—250 cm^{-1} (CsI plates) and 500—100 cm^{-1} (polythene windows) using Perkin—Elmer 457 and Beckman IR-12 spectrophotometers, respectively. No reaction between the samples and CsI plates was observed.

The Raman spectra were obtained with a Jarrel—Ash 25—300 instrument equipped with a Spectra—Physic model 165 argon ion laser, λ = 514.5 nm. The solid samples were sealed in capillary tubes, and various sensitivities and scanning times were used to examine various spectral regions.

Results and discussion

Melting points and analytical data of new compounds are given in Table 1. Tetraphenylarsonium salts have lower m.p.'s than the corresponding tetramethylammonium analoges [6]. Table 1 also contains molar conductivities measured for the tetrafluoro-, tetraazido- and tetrathiocyanato-derivatives in acetone solution. These data resemble those already reported for $M(I)[Ph_2SbX_4]$ salts [6], and behave as 1 : 1 electrolytes in this solvent.

The vibrational spectra above 600 cm^{-1} are not reported here, but are available from the author. In this region bands due to phenyl groups are present whose frequency does not depend on the particular substituent, and most of them may be identified by making reference to the well known vibrations of monosubstituted halobenzenes [14]. Of the six mass-sensitive phenyl fundamentals, those labelled *q* and *r* (in Whiffen's notation [14]) occur in this region. As their identification (for both Ph_2Sb and Ph_4As units) is uncertain, nothing can be said about their degree of splitting. For the pseudohalides, those bands which were identified as due to internal modes of N_3 and NCS groups are reported in Table 3.

The 600—100 cm^{-1} IR and Raman spectra are presented in Tables 2 and 3. A complete analysis is impossible even in those cases where both IR and Raman data are available, and most of the assignments below 250 cm^{-1} are extremely tentative. Attention has been concentrated upon making self-consistent attributions of phenyl group vibrations of Ph_2Sb and Sb—halogen(—pseudohalogen)

TABLE 2

LOW-FREQUENCY IR AND RAMAN SPECTRA (cm^{-1}) OF TETRAFLUORO- AND TETRACHLORO-DIPHENYLANTIMONATES(V)

$Ph_4As[Ph_2SbF_4]$ (I)		$Ph_4As[Ph_2SbCl_4]$ (II)		$Me_4N[Ph_2SbCl_4]$ (IIA)		Assignment
IR	Raman	IR	Raman	IR	Raman	
515vs						ν(SbF)
	496vs					
477ms	480vw	473vs				Ph_4As vibrations
465vs		461vs		463vs		*y*-mode of Ph_2Sb
		458vs		460vs		
395vw	398vw	398vw				
		391vw				
364ms	365vvw	356s	357vvw			Ph_4As vibrations
353ms	350vvw	349m(sh)				
314s						δ(SbF)
	285w					
280ms		292ms		290s		ν(SbC) (*t*)
			273vs		277vs [a]	ν(SbCl) + ν(SbC) (*t'*)
		267vs(br)		270vs(br)		ν(SbCl)
	267m					ν(SbC) (*t'*)
248s		257vs		256vs		δ(SbC) (*u*)
			247m		251mw	ν(SbC) (*t'*) + ν(SbCl)
243(sh)	245(sh)	240w	240m			Ph_4As vibrations
	238vs					ν(SbF) and Ph_4As vibrations
	229m					δ(SbC) (*u'*)
		230s		219s		δ(SbCl)
	212vs					δ(SbF)
		200vw	205m	203vw	204m	δ(SbC) (*u'*)
183mw	183m	180(sh)	183mw			Ph_4As vibrations
175m		173s	175w(sh)	173s		*x*-mode of Ph_2Sb
	144s		142ms		148m	
		129m	132ms	134m	133s	
122vw			124ms		105s	
	99s					
	83s					

[a] At $\Delta\nu = 284$ cm^{-1}, polarized, in $MeNO_2$ solution.

TABLE 3

IR (cm^{-1}) OF M[Ph_2SbX_4]

Ph_4As-[Ph_2SbBr_4] (III)	Ph_4As-[$Ph_2Sb(N_3)_4$] (IV)	Ph_4As-[Ph_2Sb-$(NCS)_4$] (V)	Ph_4As-[Ph_2SbCl_3-Br] (VI)	Me_4N-[Ph_2SbCl_3-Br] (VIA)	Ph_4As-[Ph_2SbCl_3-N_3] (VII)	Me_4N-[Ph_2SbCl_3-N_3] (VIIA)	Ph_4As-[Ph_2SbCl_3-NCS] (VIII)	Assignment
	2070vs (br)	1990vs (br)			2070s	2085s	1985s(br)	$\nu_{as}(N_3)$ or $\nu_{as}(NCS)$
	1275ms	870w (br)			1275w	1285mw		$\nu_s(N_3)$ or $\nu_s(NCS)$
	650mw							$\delta(N_3)$
	595w					600w		
	545w							
	490w							
474s	475s	476m	472m		470s		475ms	} Ph_4As vibrations
469s			470ms(sh)				470ms	
462vs	466s	466s	460s	462s	458s	463s	460s	} y-mode of Ph_2Sb
458vs	459s		455s(sh)	458s(sh)				
399vvw	395vvw							
391vvw								
356s	350vs(vbr)	362m	355ms		355s		355ms	} Ph_4As vibrations
347s		352ms	345ms		345s		345m	
						346m		$\nu(SbN_3)$
		302vs						$\nu(SbNCS)$
289ms	297s	288ms(sh)	292m	287s	294ms	291s	292m	$\nu(SbC)$ (*l*)
			267s(br)	268vs(br)	266vs(br)	270vs(br)	270s(br)	$\nu(SbCl)$
266s	259s	262s	256s	256vs(br)	257vs	258vs	256s	$\delta(SbC)$ (*u*)
250m								} Ph_4As vibrations
240w(sh)			240w		240w		240w	
	236s		229ms	220s	230s	222s	227ms	$\delta(SbX)$
226m	222ms(br)	222s(br)						
209w			207vw					
193vs(br)								$\nu(SbBr)$
			190w(br)	190mw	192w(br)	192w	190w	
	186m(br)	185mw(br)						
173m			172m	172s	173m	174ms	172mw	*x*-mode of Ph_2Sb
152mw(br)								
130mw			130vw(br)	134w(br)	130w(br)	135m(br)	130w(br)	

stretchings. In order to make allowance for the bands due to the Ph_4As group, its principal contributions in the regions around 470, 350, 250 and 180 cm^{-1} [7,9,10] (the y-, t-, u- and x-modes respectively, of the phenyl ring, in Whiffen's notation [14]), were considered. While the first two groups of vibrations were located immediately, the phenyl u- and x-modes of Ph_4As introduce some complications in spectral regions which are already fairly congested. When both Me_4N and Ph_4As were available as counter groups (compounds II—IIA, VI—VIA and VII—VIIA) features due to the latter could be identified with some confidence.

The small number of IR—Raman coincidences observed for spectra in Table 2 is taken as indicative of the presence in the solids of *trans*-$Ph_2SbX_4^-$ (X = F, Cl) species having D_{4h} skeletal symmetry. This stereochemical arrangement is not surprising in view, for instance, of the structure adopted by anhydrous Ph_2-$SbCl_3$ itself, which has been shown to exist in the solid as dimeric units where Sb has a *trans*-Ph_2Cl_4 octahedral environment [15]. $Ph_2SbX_4^-$ species with an octahedral *trans*-Ph_2 structure are also probably present in the remaining systems for which only IR data (Table 3) have been obtained.

The spectral assignments given in Tables 2 and 3 have therefore been made using the vibrational selection rules predicted for a D_{4h} *trans*-C_2SbX_4 unit, which are summarized in Table 4. The treatment of phenyl groups as being single atoms is clearly approximate, mainly because of the widely discussed fact that for phenyl derivatives there are no specific metal—phenyl stretching or bending modes. Nevertheless, spectra were assigned by assuming that the phenyl t- and u-modes of Ph_2Sb correspond to ν(SbC) and δ(SbC), respectively, and that for a *trans*-Ph_2SbX_4 species they should accordingly be split into one IR-active (t,u) and one Raman-active (t',u') component. This is possibly a fair approximation for ν(SbC), although it does not take into account the fact that the low-frequency phenyl x-mode should also contain some contribution from Sb—Ph bending. The number of bands observed below 250 cm^{-1} in the spectra of the fluoro salt (I, Table 2) perhaps indicates that the x-vibration is also split as a consequence of the local symmetry at Sb. No particular structural meaning is attached to the very small splitting of the y-vibration observed in the IR for some systems, which is attributed to solid state effects.

The IR-active antimony-halogen stretchings are identified with reasonable certainty in the majority of cases. The spectrum of compound VIIA, which is free from bands due to the cation in the 450—300 cm^{-1} range, (compare spectra IIA and VIA) allows the location of ν(Sb—N_3) at 346 cm^{-1}; for compounds IV and VII this band should be superimposed on Ph_4As absorptions. As with com-

TABLE 4

DESCRIPTION OF FUNDAMENTAL MODES AND VIBRATIONAL SELECTION RULES FOR A *trans*-C_2SbX_4 SKELETON, D_{4h} SYMMETRY

	IR-active	Raman-active
$\nu(SbC_2)$	a_{2u}	a_{1g}
$\nu(SbX_4)$	e_u	a_{1g}, b_{1g}
$\delta(SbC_2)$	e_u	e_g
$\delta(SbX_4)$	e_u	b_{2g}
$\pi(SbX_4)$	a_{2u}	

pound VIII [6], the NCS ligand coordinates through the nitrogen atom in the tetrathiocyanato derivative, V, as inferred from the frequency of internal vibration modes of NCS (Table 3). In V the corresponding ν(Sb—NCS) is thought to be responsible for the very high intensity of the envelop of bands around 300 cm^{-1}.

A decrease in the frequency of ν(Sb—hal) modes is observed on going from $PhSbhal_5^-$ [6] to $Ph_2Sbhal_4^-$ (hal = F, Cl, Br) species. This is qualitatively accounted for in terms of a weakening of the Sb—hal bonds when hal is replaced by an organic ligand, reflecting the tendency of antimony 5*s* electrons to concentrate in bonds towards the carbon at the expense of bonds towards the remaining, more electronegative, ligands. The observed ν(Sb—X) frequencies for $Ph_2SbX_4^-$ species appear very similar to those reported for corresponding Ph_3SbX_2 derivatives (X = F, Cl, Br, NCS [11], N_3 [16]).

The assignments of some skeletal frequencies in the Raman require some comments. The very intense band at $\Delta\nu = 277$ cm^{-1} of the chloro salt IIa is polarised in solution. (A nearly saturated solution of IIA in $MeNO_2$ was ~0.06 *M*. Because of the limited solubility in all suitable solvents this is the sole feature which could be examined in solution.) This band is assigned to the totally symmetric $\nu_s(SbCl_4)$ mode; however, since $\nu_s(SbC_2)$ has the same symmetry (Table 4) and is expected to occur at nearly the same energy, coupling between the two modes possibly occurs. Tentatively, the band at about 250 cm^{-1} may be assigned either to $\nu_s(SbC_2)$ (possibly coupled with $\nu_s(SbCl_4)$) or to the second antimony—chlorine stretch expected to be active in the Raman spectrum. For the fluoro salt I the totally symmetric antimony—fluorine stretching vibration is assigned at 496 cm^{-1}; because of the large energy difference between $\nu_s(SbC_2)$ and $\nu_s(SbF_4)$, the latter should be a purer vibration than $\nu_s(SbCl_4)$. Difficulties are encountered in the assignment of some prominent Raman lines of I, e.g. the bands at 238 and 212 cm^{-1}. These are very intense (Raman-active only) and have no analoges in the spectra of chloro salts. They are, therefore, attributed to modes involving antimony—fluorine motions, and have been tentatively assigned to the b_{1g} (stretching) and b_{2g} (bending) modes of the SbF_4 unit, even though their frequencies may appear to be too low for Sb—F stretching. Indeed, the relatives energies (Table 2) of these stretching and bending modes could well be reversed.

Acknowledgements

The financial support by Consiglio Nazionale delle Ricerche (Roma) is gratefully acknowledged. Thanks are given to Prof. C. Pecile (Istituto di Chimica Fisica, Universita' di Padova) for facilities in measuring far-IR and Raman spectra.

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