Journal of Organometallic Chemistry, 210 (1981) 63–67
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

ANTIMONY-121 MÖSSBAUER AND INFRARED SPECTRAL STUDY ON HALOPHENYLANTIMONATE(III) COMPOUNDS

G. ALONZO, N. BERTAZZI *, F. DI BIANCA

Istituto di Chimica Generale, Università di Palermo, Via Archirafi 26, 90123 Palermo (Italy)

and T.C. GIBB

Department of Inorganic and Structural Chemistry, The University, Leeds LS2 9JT (Great Britain)

(Received November 19th, 1980)

Summary

The synthesis and the ^{121}Sb Mössbauer and infrared spectra of the halophenylantimonates(III) $M[PhSbX_3]$ ($M = Me_4N, Ph_4As$; $X = Cl, Br, I$) are reported, and the spectral data are discussed and compared with those of SbX_4^- and other related systems. The results are in accord with the participation of the antimony 5*s* electrons in the Sb—Ph bond. In the interpretation of the electric field gradient, the contributions to V_{zz} from both the lone pair and the Sb—Ph bond electron densities are assumed to be dominant.

Introduction

Recently, ^{121}Sb Mössbauer spectroscopy has been extensively employed to study complexes of antimony(III), and this technique has proved useful, inter alia, in elucidating aspects of the structure and bonding connected with the electron lone pair on the central atom [1—4]. As part of a more general study of the coordination chemistry of mono-organoantimony(III) moieties with various ligands and their study by ^{121}Sb Mössbauer spectroscopy, we have investigated the Mössbauer spectra of phenylhalogenoantimonate(III) salts in the belief that an understanding of the relationships between spectral parameters and structural factors for these relatively simple systems might be useful in further studies on more complicated species.

The formation of organoantimony(III) halide complexes has received limited

---

* Author for correspondence.

attention. It has been known for a long time that aryldichlorostibines reacted with amine hydrochlorides or with a diazonium salt to form aryltrichloroantimonates(III), A$[ArSbCl_3]$ [5—9]. With an excess of diazonium salt, $[ArN_2^+]_2$-$[ArSbCl_4]^{2-}$ may be obtained [8,9]. An example of an iodo derivative is provided by the isolation of the dipyridinium salt of $PhSbI_3^-$ [10]. None of the reported compounds have been characterized beyond recording of their melting point or other simple properties.

In this study we have isolated chloro-, bromo-, and iodo-phenylantimonate species as tetramethylammonium or tetraphenylarsonium salts. The choice of the counter ion has been made in order to avoid as far as possible unnecessary sources of asymmetry or effects due to the presence of active hydrogens.

Present compounds are analogous to Me_4N^+ and Ph_4As^+ salts of $PhBiX_3^-$ species studied by Faraglia [11]. The two series of compounds are possibly structurally related but unfortunately no X-ray data or other structural information is available for these phenylbismuth compounds.

Experimental and results

The salt $NH_4[PbSbCl_5]$ [12] was used as the source of the monophenylantimony moiety.

The compounds $M[PhSbX_3]$ ($M = Me_4N, Ph_4As$; $X = Cl, Br$) were obtained as follows. A solution of 3 mmol of $NH_4[PhSbCl_5]$ in 20 ml of 95% EtOH was treated with 15 ml of aqueous 4 *M* HX and then with 0.5 g of solid sodium sulphite. The mixture was stirred for ten minutes after the complete dissolution of Na_2SO_3 and then treated with 4—5 mmol of the appropriate MX dissolved in the minimum volume of 4 *M* HX. After cooling for a few hours in a refrigerator the solids were filtered off and recrystallized from a 1/1 mixture of aq. conc. HX and EtOH.

The iodo derivatives $M[PhSbI_3]$ were obtained by treating a methanolic solution of the corresponding $M[PhSbCl_3]$ dropwise and with stirring with a 1/2 mixture of aq. conc. HI and MeOH. The compounds separated out immediately

TABLE 1

PHYSICAL AND ANALYTICAL DATA

Compound (colour)	M.p. (°C)	Analyses, found (calcd) (%)			
		C	H	N	X
$Me_4N[PhSbCl_3]$ (white)	143—145 (dec.)	31.46 (31.66)	4.67 (4.52)	3.80 (3.69)	28.01 (28.04)
$Ph_4As[PhSbCl_3]$ (white)	176—177 (dec.)	52.21 (52.33)	3.60 (3.66)		15.64 (15.45)
$Me_4N[PhSbBr_3]$ (pale-yellow)	154—156 (dec.)	23.49 (23.42)	3.36 (3.34)	2.84 (2.73)	46.82 (46.75)
$Ph_4As[PhSbBr_3]$ (pale-yellow)	189—191 (dec.)	43.97 (43.84)	3.14 (3.06)		30.12 (29.17)
$Me_4N[PhSbI_3]$ (orange-yellow)	192—195 (dec.)	18.15 (18.37)	2.41 (2.62)	2.24 (2.14)	58.47 (58.24)
$Ph_4As[PhSbI_3]$ (orange-yellow)	193—195 (dec.)	37.60 (37.42)	2.76 (2.62)		39.55 (39.54)

TABLE 2

MÖSSBAUER DATA AT 4.2 K

Compound	δ (mm/s)	eQV_{zz} (mm/s)	η [a]	2Γ (mm/s)	x^2/deg. of freedom
$Me_4N[PhSbCl_3]$ [b]	—14.01(3)	30.70(30)	0	2.59(6)	1.33
$Ph_4As[PhSbCl_3]$	—14.46(2)	28.84(16)	0	1.97(5)	1.05
	—14.44(2)	28.44(19)	0.17(3)	2.10(6)	0.98
$Me_4N[PhSbBr_3]$	—14.10(2)	27.20)17)	0	2.40(6)	1.21
$Ph_4As[PhSbBr_3]$	—14.36(2)	27.88(22)	0	2.08(7)	0.96
$Me_4N[PhSbI_3]$	—13.82(3)	23.71(26)	0	2.65(10)	1.16
$Ph_4As[PhSbI_3]$	—14.21(3)	24.26(27)	0	2.25(9)	1.09

[a] Zero means that η was fixed at this value. [b] The appearance of an antimony (V) component indicated that the sample had seriously decomposed when the spectrum was recorded. This spectrum was curve-fitted using a conventional summation of Lorentzian lines.

and were recrystallized from MeOH. Physical and analytical data are reported in Table 1.

Infrared spectra were recorded on Nujol mulls in the 4000—250 cm^{-1} region with a Perkin-Elmer 457 spectrophotometer. Infrared bands below 1200 cm^{-1} are reported.

$Me_4N[PhSbCl_3]$. 1185vw, 1155vw, 1062m, 1020vw, 1000w, 950ms, 920vw, 740s, 730(sh), 720(sh), 695ms, 655vw, 590—560w(vbr), 453m, 300mw [ν(Sb—Cl)], 255mw [ν(Sb—Ph)].

$Ph_4As[PhSbCl_3]$. 1185vw, 1160vw(br), 1085mw, 1065w, 1020w, 1000mw, 845vw, 735s, 725(sh), 715(sh), 685ms(br), 480mw, 475m, 465ms, 455mw, 365mw, 355mw, 345mw, 285w—275mw [ν(Sb—Cl)].

$Me_4N[PhSbBr_3]$. 1185vw, 1155vw, 1062ms, 1020vw, 1000m, 950ms, 915vw, 845vw(br), 735s, 730s, 720(sh), 695s, 685s, 670(sh), 650vw, 453m.

$Ph_4As[PhSbBr_3]$. 1185w(br), 1160w(br), 1080m, 1065mw, 1025w, 1000m, 845vw, 790mw, 750s, 740s, 730s, 685s, 480ms, 470s, 455m, 370m, 355m, 340m.

$Me_4N[PhSbI_3]$. 1155m, 1060m, 1020vw, 1000mw, 952m, 920vw, 735vs, 690s, 453m.

$Ph_4As[PhSbI_3]$. 1185m, 1165w, 1085ms, 1060w, 1025w, 1000ms, 980vw, 920vw, 850w, 840w, 745s, 740s, 735s, 690s, 680ms, 670(sh), 480ms, 470ms, 465(sh), 460m, 453m, 360ms, 345m, 260w(br) [ν(Sb—Ph)].

The ^{121}Sb Mössbauer spectra were recorded at 4.2 K using the apparatus and procedures already reported [13]. The spectra were curve-fitted using a transmission-integral method [13], with seven variable parameters: the ground-state quadrupole coupling constant eQV_{zz}, the asymmetry parameter η, the chemical isomer shift δ relative to the $Ca^{121m}SnO_3$ source, the linewidth 2Γ, the thickness T_A, and values for the intensity scaling and baseline. The final values for Mössbauer parameters are given in Table 2.

Discussion

No vibrational data can be found in the literature for monophenylantimony(III) species. The phenylantimonates(III) investigated in this work, however, show IR spectra which in the 1200—350 cm^{-1} region are very similar to those of phenylantimonates(V), M[$PhSbX_5$] (X = Cl, Br) [14], if allowance is made for an intrinsic lower resolution of vibrational features. In this region, in addition to bands arising from vibrations of the counter ions, there are bands due to internal phenyl modes of the phenylantimony unit, and can all be assigned following the assignments already given for M[$PhSbX_5$] compounds [14].

Below 350 cm^{-1} and within the 250 cm^{-1} instrumental lower limit, among skeletal Sb—phenyl and Sb—halogen stretching and bending modes only ν(Sb—Ph) and ν(Sb—Cl) bands are expected to occur in practice. The comparison of spectra of various halide salts permits the assignments indicated with the experimental data in the previous section, showing that these modes are at lower energy than in corresponding $PhSbX_5^-$ species. The observed shifts are probably a consequence of the presence of the lone pair electrons and can be qualitatively accounted for in terms of a weakening of both Sb—Ph and Sb—Cl(X) bonds due to the tendency of Sb 5*s* electrons to concentrate in the lone pair orbital.

It should be noted that ν(Sb—Cl) is lower than ν(Te—Cl) in the related $PhTeCl_3$ derivative [15]. This observation is in line with the expected bathochromic shift associated with the addition of negative charge in an isoelectronic series of chloro species [16].

The Mössbauer isomer shifts are in the range observed for antimony(III) compounds as, for example, in the corresponding SbX_3 and A[SbX_4] (A = pyH, R_4N) derivatives [2, 3 and references therein]. However, a definite increase of δ can be noticed with respect to SbX_4^- species. This implies a lower *s*-electron density at Sb in the case of the $PhSbX_3^-$ species, since the $\Delta R/R$ nuclear factor for ^{121}Sb is negative. The same effect can be observed between $SbCl_3$ and $MeSbCl_2$, and along the methylchlorostibines series the increase of δ continues with Me_2SbCl and Me_3Sb [17]. Although possible differences in structure may be important, such an increase in δ seems attributable to the substitution of a halide by an organic ligand. Since for antimony(III) compounds the *s*-electron density at the nucleus is mainly dictated by the *s*-character of the lone pair, the observations for $PhSbX_3^-$ can be explained in terms of some withdrawal of *s*-character from the lone pair and use in the Sb—Ph bond.

A further point to be noted is that δ values for M[$PhSbX_3$] show a less marked dependence (if any) on the nature of X than in the corresponding A[SbX_4]. For the latter compounds a small but noticeable increase of δ can be observed as X is changed from Cl to I, and this has been attributed to a deshielding effect on the *s*-density caused by a *p*-electron withdrawal along the Sb—X bonds [2,3]. If in SbX_4^- and $PhSbX_3^-$ the coordination number and stereochemistry are similar, Sb—X bonds in $PhSbX_3^-$ must be considered to be even more ionic in character and the *p*-deshielding effect is expected to be maintained. An hypothesis which can be put forward (very tentatively in view of the absence of structural data) is that the amount of *s*-electron character transferred from the lone pair to the Sb—Ph bond decreases slightly going from Cl to I. Such a process would clearly have the opposite effect to changes in the electron-withdrawing ability of X in the Sb—X bond, and act as a buffer for the *s*-density at Sb.

The e.f.g. parameters are characterized by (i) a large and positive eQV_{zz}, (ii) a small value of the asymmetry parameter (the best candidate for showing a measurable η being the $PhSbCl_3^-$ species), and (iii) a dependence of eQV_{zz} on X in the order Cl > Br > I.

In the interpretation of Mössbauer data for SbX_4^- and other inorganic Sb^{III} species a dominant negative contribution of the lone pair to V_{zz} has been generally assumed. In the present case we must consider also a substantial contribution to V_{zz} from the Sb—Ph bond. If the two contributions (from the lone pair and the Sb—Ph bond electron densities) were of about the same magnitude, only a large angle between their directions could account for the large eQV_{zz} and low η observed.

These considerations are in line with point-charge model calculations of the electric field gradient tensor [18] for the most probable structures which can be suggested for the present phenylantimonates(III), i.e. monomeric ψ-tbp species having the lone pair and Ph in the equatorial plane, or polymeric species (dimers of chain polymers through halogen bridging) featuring a ψ-octahedral environment about Sb with the lone pair and Ph in *trans*-positions. The results of these calculations show also that negative contributions to V_{zz} from the Sb—X bonds in the order I > Br > Cl, significantly smaller than those due to the lone pair and Sb—Ph, can rationalize the observed dependence of eQV_{zz} on the halide ligand. As expected, the principal difference between the two structural types is in the η value. The latter being zero for the ψ-octahedral case, and finite for a ψ-tbp structure. The small η shown by $Ph_4As[PhSbCl_3]$ may perhaps arise from such a stereochemistry, but it would be unwise to rely only on this evidence in drawing structural conclusions.

Acknowledgement

This work was supported by CNR (Rome).

References

1 J.D. Donaldson, M.J. Tricker and B.W. Dale, J. Chem. Soc. Dalton, (1972) 893.
2 J.D. Donaldson, J.T. Southern and M.J. Tricker, J. Chem. Soc. Dalton, (1972) 2637.
3 J.G. Ballard, T. Birchall, J.B. Milne and W.D. Moffett, Canad. J. Chem., 52 (1974) 2375.
4 T. Birchall and B. Ducourant, J. Chem. Soc. Dalton, (1979) 131.
5 P. Pfeiffer and K. Schneider, Ber., 68 (1935) 50.
6 P. Pfeiffer and P. Schmidt, J. Prakt. Chem., 152 (1939) 27.
7 A.B. Bruker, Zh. Obshch. Khim., 6 (1936) 1823.
8 A.B. Bruker and E.S. Makhlis, Zh. Obshch. Khim., 7 (1937) 1880.
9 A.B. Bruker, Zh. Obshch. Khim., 18 (1948) 1297.
10 W.R. Roper and C.J. Wilkins, Inorg. Chem., 3 (1964) 500.
11 G. Faraglia, J. Organometal. Chem., 20 (1969) 99.
12 H. Schmidt, Liebigs Ann. Chem., 421 (1920) 174.
13 N. Bertazzi, T.C. Gibb and N.N. Greenwood, J. Chem. Soc. Dalton, (1976) 1153.
14 N. Bertazzi, M. Airoldi and L. Pellerito, J. Organometal. Chem., 97 (1975) 399.
15 W.R. McWhinnie and P. Thavornyutikarn, J. Chem. Soc. Dalton, (1972) 551.
16 I.R. Beattie, F.C. Stokes and L.E. Alexander, J. Chem. Soc. Dalton, (1973) 465.
17 J.G. Stevens, J.M. Trooster and H.A. Meinema, J. Phys. (Paris) Coll., 41, C1 (1980) 233.
18 R. Barbieri, N. Bertazzi, T.C. Gibb, H.A. Meinema and J.G. Noltes, J. Chem. Soc. Dalton, (1979) 1925.