CRYSTAL STRUCTURES OF $Bu_4[PhSbBr_2Cl]$ AND $Bu_4N[Ph_2SbBr_2]$

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Abstract

Crystal structures have been determined for $Bu_4N[PhSbClBr_2]$ (1) and $Bu_4N[Ph_2SbBr_2]$ (2). In solid (1) the anion exists as a dimer with antimony in a distorted square pyramidal geometry while in (2) the anion exists as a monomeric species and has a see saw structure(pseudo trigonal bipyramidal with one position occupied by a lone pair).

Introduction

There are a number of reports on the formation of haloanions $[SbX_4]^-$, $[Sb_2X_9]^-$ or $[SbX_5]^{2-}$ by successive addition of halide ions , and their structures have been determined [1,2]. Replacement of one or more of the halo atoms by phenyl groups will give Ph_nSbCl_{3-n} with reduction of antimony lewis acidity. Organoantimony(III) compounds like $PhSbX_2$ and Ph_2SbX ought to act as electron acceptors like SbX_3, albiet to a lesser extent . On reaction of X^- with $PhSbX_2$, $[PhSbX_3]^-$ is formed (X = Cl, Br or I) and the reaction of Cl^- with Ph_2SbCl is reported to form $[Ph_2SbCl_2]^-$ [3,4]. In continuation of our interest in mixed haloaryl-antimonates(III) viz. $R_4N[PhSbX_2Y]$ and $R_4N[Ph_2SbXY]$ from $PhSbX_2$ and Ph_2SbX where $X \neq Y$ = halide [5,6], we are now reporting the crystal structures of $Bu_4N[PhSbClBr_2]$ (1) and $Bu_4N[Ph_2SbBr_2]$ (2)

Experimental

IR spectra were recorded in KBr on Nicolet Magna 750 spectrometer. Melting points are uncorrected.

$Bu_4N[PhSbClBr_2]$ (1) : This was prepared according to published procedure [6] and the product was recrystallised from methanol; m.p. 125^0 C and its IR spectrum was compared with that in the literature [5].

$Bu_4N[Ph_2SbBr_2]$ (2) : The complex was synthesised by disproportionation of $Bu_4N[Ph_2SbClBr]$. 1 mmol of Bu_4NBr was dissolved in anhydrous methanol (15ml) and it was added to a methanolic solution of Ph_2SbCl (1 mmol). The mixture was stirred at room temperature to yield $Bu_4N[Ph_2SbClBr]$. The complex was filtered and washed with methanol and ether, then it was dissolved in toluene and stirred for one hour at 70°C,when the disproportionation reaction takes place. $Bu_4N[Ph_2SbCl_2]$ and $Bu_4N[Ph_2SbBr_2]$ were obtained as the products of the reaction. $Bu_4N[Ph_2SbBr_2]$ was crystallised from methanol ; m.p. = 142°C and its IR and PMR were compared with the published spectra[6].

Crystal X- ray structure determination : Data were collected on a Siemens P4\Pc diffractometer at 293°K using monochromated Mo-Kα radiation (λ = 0.7107). The system used for calculations was Siemens SHLEXTL PLUS (PC Version) and structure determination by direct methods and refinement by a full matrix least squares procedure. Atomic coordinates, equivalent isotropic and anisotropic displacement cofficients have been deposited. Crystal data are given in Table 1.

Table 1. Crystal data for $Bu_4N[PhSbClBr_2]$ (1) and $Bu_4N[Ph_2SbBr_2]$ (2).

Compound	$Bu_4N[PhSbClBr_2]$	$Bu_4N[Ph_2SbBr_2]$
Molecular Wt.	1273.2	678.2
Empirical Formula	$C_{44}H_{82}Br_4C_{12}N_2Sb_2$	$C_{28}H_{46}Br_2NSb$
Crystal System	Monoclinic	monoclinic
Space Group	$P2_1/n$	C2/c
a, Å	10.237(1)	12.038(1)
b, Å	17.156(3)	13.575(1)
c, Å	15.736(2)	18.811(2)
β, °	90.64(1)	101.476(8)
Z	2	4
D_c, g cm^{-3}	1.530	1.495
Crystal size, mm	0.40 × 0.36 × 0.22	0.38 × 0.36 × 0.06
Volume, Å^3	2763.6(7)	3012.5(6)
F(000)	1272	1296
μ, cm^{-1}	39.94	35.84
Scan type	ω	ω
2θ Range	3.0 to 50.0°	3.0 to 50.0°
Scan speed	Variable; 3.0 to 60.0°/min	Variable; 4.0 to 100.0°/min
Independent reflections	4868(R_{int}= 0.033)	2657(R_{int}= 0.028)
No. of unique reflections	2117 [$F > 5.0\sigma(F)$]	1511 [$F < 4.0\sigma(F)$]
$\Delta_{\rho\,max}$, $\Delta_{\rho\,min}$ e Å^{-3}	2.00, -0.92	0.85, -0.84
R	0.069	0.058
R_w	0.090	0.065
GOF	1.31	1.47

Results and discussion

Crystal structure of $Bu_4N\,[PhSbClBr_2]$: The molecular structure of (1) and the atom numbering system are shown in Figure1. Selected bond lengths and bond angles and atomic coordinates are reported in Table 2 and 3 respectively.

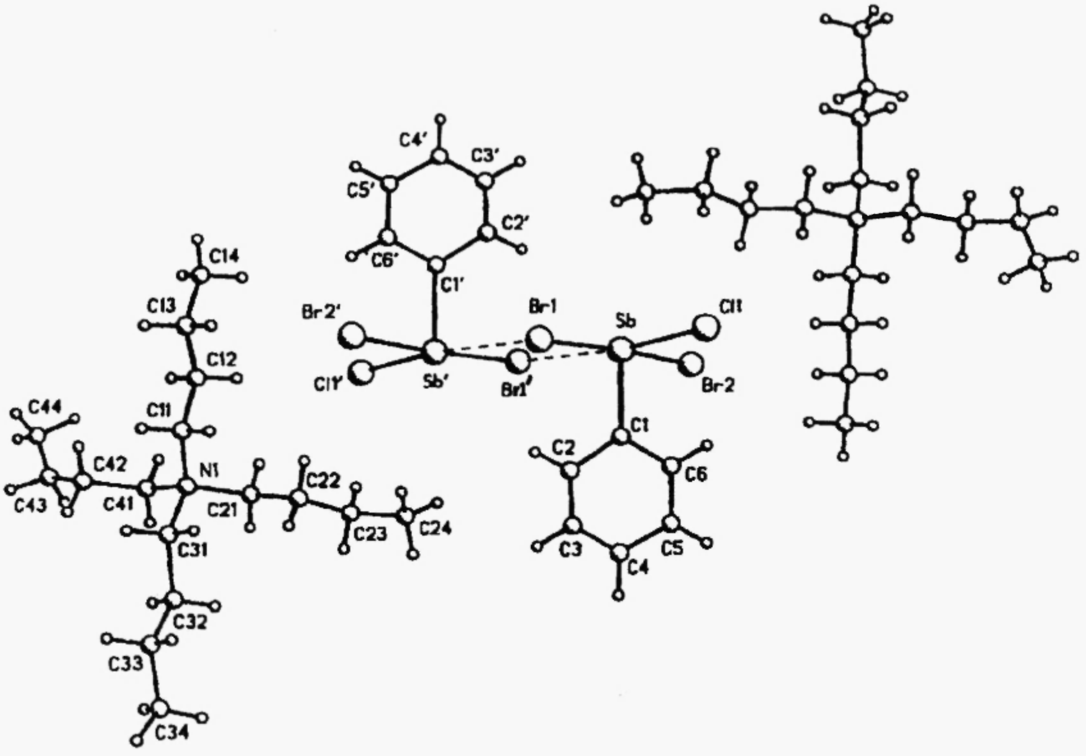

Figure 1.

In the anion the geometry about antimony is essentially square pyramidal and the molecule exists as a dimer in contrast to the compound (2). The Sb-Br(1) bond length is slightly longer than Sb-Br(2) bond length owing to the participation of Br(1) atom in bridging. The Phenyl group is at the apical position of the square pyramid and the three bromine atoms and one chlorine atom form the basal plane of the system, similar to $[PhSbCl_3]^-$or $[SbCl_4]^-$ [4,7]. In the dimer the two phenyl groups occupy anti-position to each other thereby minimising repulsion. The tetrahedral cation has no interaction with the anion . The cation has angles in the 107.5° to 112.2° range and a mean C-N distance of 1.516Å. There are no unusal features associated with phenyl group. The Sb-Cl (2.545Å) distance found in compound (1) is clearly greater than the statistically determined single bond distance 2.32Å [8]. Similarly $[PhSbCl_3]^-$ anion reported by Sowerby *et al* [4] also exists as a dimer.

Table 2. Selected Bond Lengths(Å) and Bond Angles (°) for Compound (1).

Sb(1) - Br(1)	2.925(3)	Sb(1) - Br(1′)	3.168(3)
Sb(1) - Cl(1)	2.545(4)	Sb(1) - C(1)	2.14(1)
Sb(1) - Br(2)	2.650(3)	N(1) - C(21)	1.56(2)
N(1) - C(11)	1.49(2)	N(1) - C(41)	1.51 (2)
N(1) - C(31)	1.53(2)		
Br(1)-Sb(1)-Br(1′)	86.70(8)	Br(2)-Sb(1)-Cl(1)	90.8(1)
Br(1)-Sb(1)-Cl(1)	89.2(1)	Br(1)-Sb(1)-C(1)	87.0(5)
Br(1)-Sb(1)-C(1)	87.0(5)	C(1)-Sb(1)-Cl(1)	93.0(5)
Br(1)-Sb(1)-Br(2)	176.3(1)	Sb(1)-C(1)-C(6)	122.3(14)
Sb(1)-C(1)-C(2)	122.6(13)	C(11-N(1)-C(21)	111.8(16)
C(21)-N(1)-C(31)	109.1(16)	C(21)-N(1)-C(41)	107.8(15)
C(11)-N(1)-C(31)	107.5(15)	C(11)-N(1)-C(41)	112.2(16)
C(31)-N(1)-C(41)	108.3(15)		

Crystal structure of Bu_4N $[Ph_2SbBr_2]$: The molecular structure of compound (2) and the numbering system are shown in Figure 2. The selected bond lengths and bond angles and atomic coordinates are given in Tables 4 and 5. The anion $[Ph_2SbBr_2]^-$ exists as a monomeric species and not as a dimeric species as found in compound (1) and has a see-saw structure (pseudo trigonal bypyramidal with one position occupied by a lone pair). The two phenyl groups are in equatorial positions while the two bromine atoms are in axial positions. Considering the axial angle Br(1)-Sb-Br(2) = 174.7(1) and the equatorial and equatorial/axial bond angles, it can be inferred that there is large distortion in the antimony polyhedron. The two Sb-C distances are equivalent and are equal, similarly the two Sb-Br distances are equivalent and are of same length. But in the crystal structure of

$Me_4N[Ph_2SbCl_2]$ the two Sb-C and Sb-Cl bond distances differ slightly among themselves [4]. Similarly in the crystal structure of related compound viz. $Ph_4P[Ph_2SbBr_2]$ the two Sb-Br distances differ slightly in length and the mean bond distance (2.786Å) which is higher than the mean bond distance found for the title compound (2.764Å) [9]. The Sb-Br bond distance is slightly shorter than the distance found in the anion(1). As in the compound (1) there is absence of close intermolecular contacts. The dimensions of the cation and phenyl groups present no special features.

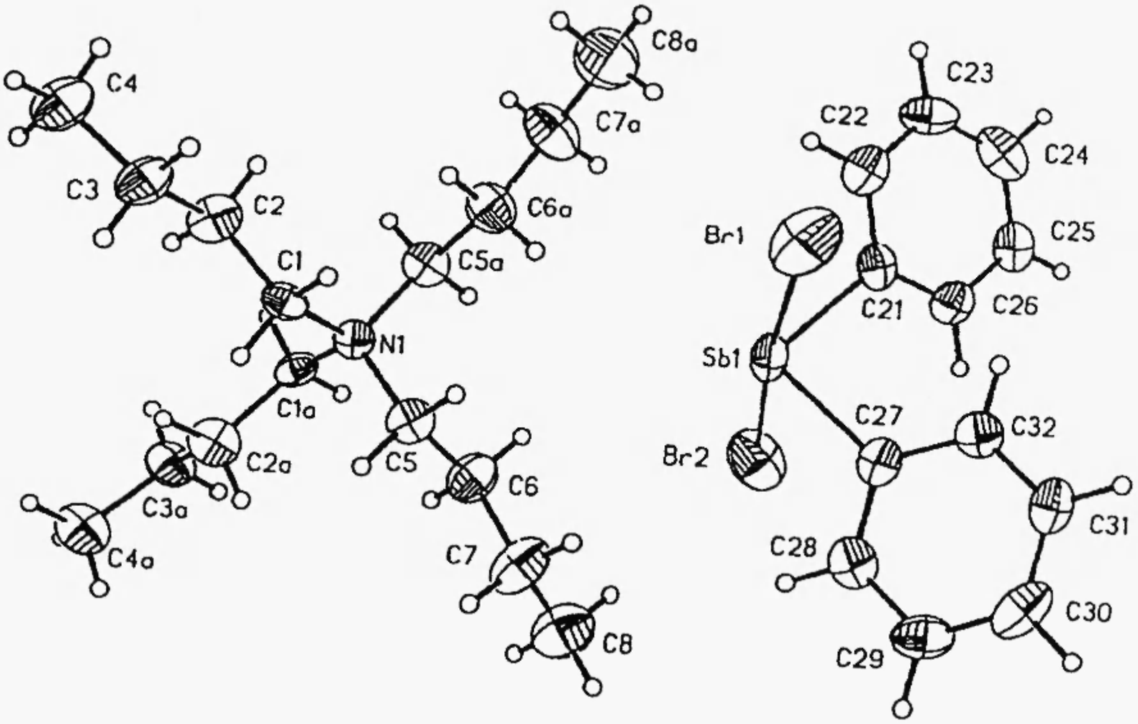

Figure. 2.

Table 3. Atomic coordinates (x10^4) and equivalent isotropic displacement coefficients (Å^{2}x10^3) for compound (1)

	x	y	z	U(eq)
Sb	-6271(1)	6005(1)	-326(1)	60(1)
Br(1)	-5940(2)	5015(2)	1175(2)	85(1)
Br(2)	-6469(3)	6968(2)	-1638(2)	111(1)
Cl(1)	-8198(4)	6665(2)	387(3)	48(1)
C(1)	-4884(18)	6777(11)	249(11)	59(6)
C(2)	-3637(19)	6521(11)	552(14)	74(8)
C(3)	-2831(23)	7027(15)	933(16)	87(9)
C(4)	-3085(29)	7764(18)	1036(16)	98(11)
C(5)	-4223(27)	8058(13)	727(14)	83(9)
C(6)	-5116(21)	7570(13)	331(13)	76(8)
N(1)	1547(15)	2584(10)	1961(10)	70(6)
C(11)	390(18)	2100(12)	2175(12)	70(7)
C(12)	-341(19)	1724(14)	1445(15)	82(9)
C(13)	-1406(22)	1213(14)	1749(16)	87(9)
C(14)	-2133(25)	857(17)	1041(19)	114(13)
C(21)	1166(25)	3297(14)	1398(12)	85(9)
C(22)	240(22)	3860(13)	1790(17)	89(9)
C(23)	132(29)	4532(19)	1222(23)	137(16)
C(24)	-848(34)	5246(21)	1526(27)	179(22)
C(31)	2145(22)	2874(13)	2794(12)	76(8)
C(32)	3318(21)	3450(16)	2761(15)	90(10)
C(33)	3805(31)	3611(16)	3641(22)	122(14)
C(34)	4868(24)	4223(16)	3650(17)	106(12)
C(41)	2575(21)	2123(14)	1494(13)	78(8)
C(42)	3071(33)	1405(17)	1915(22)	131(15)
C(43)	3954(38)	921(19)	1355(29)	165(21)
C(44)	3330(49)	405(22)	1052(40)	320(54)

*Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Selected bond lengths and bond angles for Bu$_4$N[Ph$_2$SbBr$_2$]

Sb-Br(1)	2.764(2)	Br(1)-Sb-C(21)	87.7(2)
Sb-Br(2)	2.764(2)	Br(2)-Sb-C(21)	88.8(3)
Sb-C(21)	2.16(1)	C(21)-Sb-C(27)	96.6(6)
Sb-C(27)	2.16(1)	Br(1)-Sb-Br(2)	174.7(1)
N-C(1)	1.48(1)	Br(2)-Sb-C(27)	87.7(2)
N-C(1A)	1.48(1)	Br(1)-Sb-C(27)	88.8(3)
N-C(5)	1.52(1)	C(1)-N-C(5A)	112.9(5)
N-C(5A)	1.52(1)	C(1)-N-C(5)	105.2(5)

Table 5. Atomic coordinates (x10^4) and equivalent isotropic displacement coefficients (Å^{2}x10^3) for compound (2)

	x	y	z	U(eq)
Sb(1)	0	3661(1)	2500	50(1)
Br(1)	1968(1)	3754(1)	3545(1)	94(1)
Br(2)	-1968(1)	3754(1)	1455(1)	94(1)
C(21)	-724(8)	4719(7)	3135(6)	43(4)
C(22)	-732(9)	4535(8)	3863(7)	53(4)
C(23)	-1213(9)	5187(10)	4277(7)	57(5)
C(24)	-1670(9)	6033(9)	3973(8)	62(5)
C(25)	-1703(8)	6235(8)	3247(7)	52(4)
C(26)	-1239(9)	5573(7)	2835(7)	47(4)
N(1)	0	-500(8)	2500	37(4)
C(1)	957(9)	-1124(6)	2865(5)	39(3)
C(2)	731(9)	-1878(9)	3416(7)	54(4)
C(3)	1776(10)	-2433(9)	3753(7)	57(4)
C(4)	1575(10)	-3260(9)	4246(7)	66(5)
C(5)	487(8)	137(7)	1975(6)	45(4)
C(6)	-345(10)	760(9)	1458(7)	59(5)
C(7)	233(10)	1307(11)	926(8)	74(5)
C(8)	-582(16)	1799(13)	317(9)	105(8)

*Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.
Symmtry code x,y,z,→ -x,y, 0.5-z.

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