SHORT PAPER

J. Chem. Research (S),
2000, 198–199

[Tetra(*n*-butyl)ammonium] [di(μ-bromo) bis{dichloro(*p*-tolyl)antimonate(III)}]: synthesis and crystal structure[†]

Ajai K. Singh[a]*, C.V. Amburosea, N. K. Jha[a], P. Sharma[b], A. Cabrera[b] and G. E-Perz[b]

[a]*Department of Chemistry, Indian Institute of Technology, New Delhi 110 016, India*
[b]*Instituto de Quimica, UNAM, Circuito Exterior, Coyoacan, D.F. 04510, Mexico*

The crystal structure of a salt of mixed trihalo(aryl)antimonate(III) anion, $[n\text{-}Bu_4N]_2[(p\text{-tol})Cl_2Sb(\mu\text{-}Br)_2SbCl_2(p\text{-tol})]$ (*p*-tol = *p*-tolyl) reveals that the anion is dimeric in nature and two Sb atoms of the dimer are asymmetrically bridged by bromide ions (Sb-Br(bridging) = 2.985(2) / 3.373(1) Å).

The SbX_3 (X = halide) acts as a Lewis acid and forms a complex anion on reaction with halide ions, even when one X is substituted by an alkyl or aryl group. Such complex anions $[PhSbCl_3]^-$ and $[p\text{-tolSbCl}_3]^-$ (*p*-tol = *p*-tolyl) are characterized[1,2] structurally as salts of tetraalkylammonium ions and reported to have dimeric structures which containing two Sb atoms bridged by a pair of chlorides. On the other hand the structural characterization of mixed trihalo(aryl)antimonate (III) anion is very rare[3] but they are also reported to be dimeric. However, to make generalization about the halides ions involved in the bridging of two Sb atoms of the dimeric unit, structural characterization of several mixed trihalo(aryl)antimonate(III) anions, having different combinations of halide ions and organic groups, is necessary.

$$R_4\,NY + p\text{-tolSbX}_2 \longrightarrow [R_4N][p\text{-tolSbX}_2\,Y]$$

p-tol = *p*-toly; R = Et, *n*-Pr, *n*-Bu or *n*-Pe
X = CI, Y = Br or I; X = Br, Y= 1

We have synthesized seven salts (Table 2) of three mixed trihalo(aryl)-antimonate(III) anions (equation (1) having compositions $[p\text{-tolSbCl}_2X]^-$ (X = Br or I; *p*-tol = *p*-tolyl) and $[p\text{-tolSbBr}_2I]^-$ but crystals suitable for X-ray diffraction could be grown for $[n\text{-}Bu_4N][p\text{-tolSbCl}_2Br]$ only. It is found to be $[n\text{-}Bu_4N]_2[(p\text{-tol})Cl_2Sb(\mu\text{-}Br)_2SbCl_2(p\text{-tol})]$, dimeric with asymmetric bromo bridges (molecular structure shown in Fig 1.) and described here in detail. The selected bond lengths and angles are given in Table 1. The Sb(1)–Cl(2) being *trans* to Sb(1)–Br(1) is longer than Sb(1)–Cl(1) which is *trans* to the long bridging Sb–Br. The Sb(1)–C(21) (2.169(10) Å) is slightly longer than Sb–C distances reported for $[PhSbCl_3]^-$ (2.12(1) Å)[1], $[p\text{-tolSbCl}_3]^-$ (2.155(3) Å)[2a] and other Sb–C single bond (2.090(13) – 2.175(6) Å).[5,6] The geometry around antimony may be described as tetragonal pyramidal or pseudo octahedral. The *p*-tolyl groups in the dimeric unit are in apical position with respect to $Sb_2Cl_4Br_2$ plane and *trans* to each other. Out of halide ions Cl^- and Br^-, the later one is used for bridging Sb in the present mixed trihalo(aryl)–antimonate(III) anion as reported earlier[3] for similar species. The structures of $n\text{-}Bu_4N$ cation (C–N = 1.529(6) Å, C–C = 1.45(1) Å; C–N–C, N–C–C and C–C–C 109.5(1), 116.6(1) 114.2(5)°) and p-tolyl groups (C–C (av.) = 1.37(6) Å and C–C–C angle = 120.0(1)°) are normal.

Experimental

The *p*-tolylantimony dichloride[4] was synthesised by the published method. ^1H NMR spectra were recorded on a Bruker Spectrospin DPX 300 NMR spectrometer at 300.1316507 MHz. The C, H and N analyses were carried out on Perkin Elmer elemental analyser 240 C. The tetraalkylammonium salts of mixed trihalo(aryl)antimonate(III) may be synthesised by the procedure similar to the one given below for $[n\text{-}Bu_4N]_2[(p\text{-tol})Cl_2Sb(\mu\text{-}Br)_2SbCl_2(p\text{-tol})]$.

Synthesis of $[n\text{-}Bu_4N]_2[(p\text{-tol})Cl_2Sb(\mu\text{-}Br)_2SbCl_2(p\text{-tol})]$: Tetra-*n*-butylammonium bromide (1.612 g 5 mmol) and *p*-tolylantimony dichloride (1.418, 5 mmol) were dissolved separately in 15 ml of anhydrous ethanol. The two solutions were mixed together with stirring under nitrogen atmosphere at room temperature and the mixture was stirred for 40 min. The resulting white precipitate was filtered, washed with small amounts of ethanol and dry diethyl ether successively and dried *in vacuo*. Its crystals suitable for X-ray diffraction were obtained from acetone. Yield ~ 85 %; mp 149 °C ; molar conductance 124.5 $ohm^{-1}\,cm^2\,mol^{-1}$. Analyses: Found: C, 46.02; 6.94; N, 2.26 %; $C_{23}H_{47}NSbCl_2Br$ requires C, 45.54; H, 7.10; N, 2.31 %. NMR(^1H, $CDCl_3$, 25 °C) : δ, 0.89–1.03 (t, 12H, CH_3 of *n*-Bu), 1.20–1.71 m, 16H, two middle CH_2 of *n*-Bu), 2.35 (s, 3H, CH_3 of *p*-tolyl), 3.06–3.23 (t, 8H, NCH_2)7.23–7.31 (d, 2H, ArH, *m* to Sb), 8.14–8.23 (d, 2H, ArH, *o* to Sb); ($^{13}C\{^1H\}$, $CDCl_3$, 25 °C) δ, 13.5 (CH_3), 19.5 (CH_2 linked to CH_3), 21.3 (CH_3 of *p*-tolyl), 23.8 (middle CH_2), 58.6(NCH_2), 128.7 (C *m* to Sb), 134.3 (C *o* to Sb), 138.4 (C *ipso* to Sb), 153.6 (C *p* to Sb).

X-ray analysis: The Siemens P4/PC X-ray diffractometer was used for the data collection using graphite monochromated Mo–Kα radia-

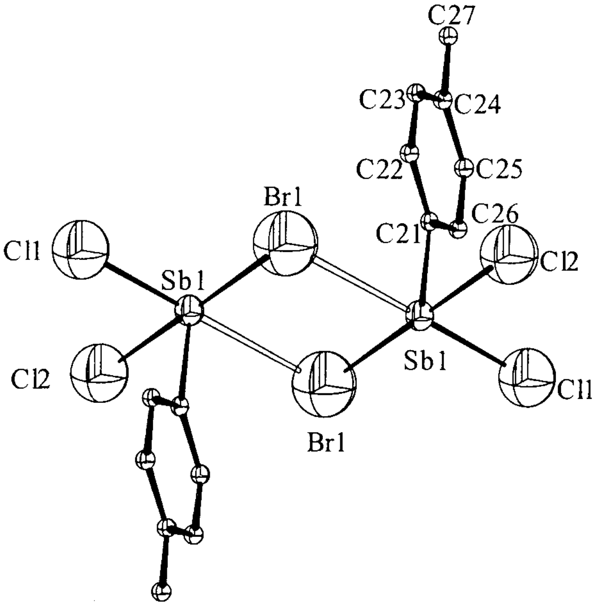

Fig. 1 Molecular structure $[(p\text{-tol})Cl_2Sb(\mu\text{-}Br)_2SbCl_2(p\text{-tol})]^-$

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*To receive any correspondence: E-mail: aksingh@chemistry.iitd.ernet.in.

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Selected bond lengths (Å) and bond angles (°)

Bond length (Å)			
Sb(1)–Cl(1)/Sb(1a)–Cl(1a)	2.519(3)	Sb(1)–Cl(2)/Sb(1a)–Cl(2a)	2.637(3)
Sb(1)–Br(1)/Sb(1a)–Br(1a)	2.985(2)	Sb(1)–Br(1a)/Sb(1a)–Br(1)	3.091(3)
Sb(1)–C(21)	2.169(10)	Sb(1a)–C(21a)	2.169(10)
Sb(1)–Sb(1a)			4.31(8)
Bond angles (°)			
Cl(1)–Sb(1)–C(21)	91.6(3)	Cl(2)–Sb(1)–C(21)	90.6(3)
Br(1)–Sb(1)–C(21)	87.3(3)	Br(1)–Sb(1)–Cl(1)	88.1(1)
Br(1)–Sb(1)–Cl(2)	177.3(7)	Br(1)-Sb(1)–Br(1a)	89.4(3)
Cl(2)–Sb(1)–Br(1a)	92.2(7)	Br(1a)–Sb(1)–C(21)	87.7(6)
Cl (1)–Sb(1)–Br(1a)	177.4(5)		

Table 2 Analytical and ^{1}H NMR in CDCl$_3$) data of [R$_4$N] [p-tolSbX$_2$Y]

S. N.	Compound (mp, ° C)	Analysis % found (calculated) C	H	N	Chemical shift (δ, ppm)
1.	[Et$_4$N][p-tolSbCl$_2$Br] (162)	36.88 (36.46)	5.51 (5.47)	2.73 (2.73)	1.24 (t, 12H, H$_2$), 2.37 (s, 3H, CH$_3$ of p—tol), 3.20(q, 8H, H1), 7.29 (d, 2H, ArH *m* to Sb), 8.19 (d, 2H, ArH *o* to Sb)
2.	[*n*-Pr$_4$N][p-tolSbCl$_2$I] (152)	38.30 (38.19)	6.03 (5.86)	2.48 (2.35)	1.01 (t, 12H, H$_3$), 1.67 (m, 8H, H$_2$), 2.37 (s, 3H, CH$_3$ of *p*-tol), 3.17 (t, 8H, H$_1$), 7.26 (d, 2H, ArH *m* to Sb), 8.18(d, 2H, ArH *o* to Sb)
3.	[*n*-Pr$_4$N][*p*-tolSbBr$_2$I] (138)	32.94 (33.24)	4.91 (5.10)	1.96 (2.04)	1.07 (t, 12H, H$_3$), 1.73 (m, 8H, H$_2$), 2.38 (s, 3H, CH$_3$ of *p*-tol), 3.22 (t, 8H, H$_1$), 7.24 (d, 2H, ArH *m* to Sb), 8.12 (d, 2H, ArH *o* to Sb)
4.	[n-Bu$_4$N][p-tolSbCl$_2$I] (152)	42.22 (42.26)	6.38 (6.58)	2.11 (2.14)	1.00 (t, 12H, H$_4$), 1.48 (m, 16H, H$_2$ + H$_3$), 2.34 (s, 3H, CH$_3$ of *p*-tol), 3.20 (t, 8H, H$_1$), 7.21 (d, 2H, ArH *m* to Sb), 8.24 (d, 2H, ArH *o* to Sb)
5.	[n-Bu$_4$N][*p*-tolSbBr$_2$I] (158)	39.93 (37.19)	6.07 (5.79)	1.91 (1.89)	1.04(t, 12H, H$_4$), 1.53 (m, 16H, H$_2$ + H$_3$), 2.34 (s, 3H, CH$_3$ of *p*-tol), 3.24 (t, 8H, H$_1$), 7.28 (d, 2H, ArH *m* to Sb), 8.24 (d, 2H, ArH *o* to Sb)
6.	[n-Pe$_4$N][p-tolSbCl$_2$Br] (103)	48.61 (48.95)	7.88 (8.01)	2.06 (2.12)	0.92(t, 12H, H$_5$), 1.44 (m, 24H, H$_2$ + H$_3$ + H$_4$), 2.34 (s, 3H, CH$_3$ of *p*-tol), 3.13 (t, 8H, H$_1$), 7.26 (d, 2H, ArH *m* to Sb), 8.20 (d, 2H, ArH *o* to Sb)

n-Pe = -CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$; *n*-Bu = -CH$_2$CH$_2$CH$_2$CH$_3$; *n*-Pr = -CH$_2$CH$_2$CH$_3$; Et = -CH$_2$CH$_3$
1 2 3 4 5 1 2 3 4 1 2 3 1 2

tion (λ = 0.71073 Å) employing ω–2θ technique. Semi-Empirical absorption correction was applied The structure was solved using by routine heavy atom/ Fourier methods (using SHELXTL PLUS (PC Version)^7) and refined by full matrix least squares on F^2. The crystal data are as follows.

Chemical formula: C$_{23}$H$_{47}$NSbCl$_2$Br, formula weight: 669.27, temperature: 293(2) K; crystal system: monoclinic; space group: P2(1)/n; μ (mm^{-1}) 8.028; unit cell dimension: a = 9.786(2) Å, b = 20.968(2) Å, c = 14.307(4) Å; α = 90° β = 109.7(6)°, γ = 90°; volume: 2762.8(10) Å^3; z = 4; reflections collected 5107; independent reflections 4810 (Rint 0.0492); Final R indices [$I > 2\sigma(I)$]: R1 = 0.0631, wR2 = 0.1609.

Received 24 November 1999; accepted 22 March 2000
Paper 99/24

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