Short Communication

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Preparation and molecular structure of the dimeric arylstibonic monoethylester [2,6-$Mes_2C_6H_3Sb(O)(OEt)(OH)]_2$

Abstract: Heating of the arylstibonic acid $[2,6\text{-}Mes_2C_6H_3Sb(O)(OH)_2]_2$ in refluxing ethanol gave rise to the esterification and formation of the monoethyl ester $[2,6\text{-}Mes_2C_6H_3Sb(O)(OEt)(OH)]_2$, the molecular structure of which was established by X-ray crystallography.

Keywords: antimony; esterification; stibonic acid.

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Despite being known for more than 100 years (Hasenbäumer, 1898), the chemistry of arylstibonic acids began to develop at a rapid pace only within the last 5 years. For a long time, progress in the field has arguably been delayed by the fact that most previously known arylstibonic acids are high-melting amorphous polymers that are only poorly soluble in most common solvents.

However, recently, the research groups of Winpenny (Baskar et al., 2007; Ali et al., 2008), Nicholson (Clark et al., 2009; Nicholson et al., 2010, 2011, 2012), Kortz (Piedra-Garza et al., 2009), and Baskar (Prabhu et al., 2009; Jami et al., 2010; Jami and Baskar, 2012) developed powerful strategies to build up discrete clusters and well-defined polyoxometalates based on arylstibonic acids by breaking down the random polymeric structures into smaller aggregates or by generating mononuclear arylantimony oxo moieties *in situ* using aryl cleavage reactions. Our strategy to avoid extensive aggregation in arylstibonic acids involved the kinetic stabilization provided by a bulky *m*-terphenyl substituent. Thus, the controlled base hydrolysis of $2,6\text{-}Mes_2C_6H_3SbCl_4$ provided the dimeric arylstibonic acid $[2,6\text{-}Mes_2C_6H_3Sb(O)(OH)_2]_2$ as crystalline material after recrystallisation from THF (Beckmann et al., 2008). The reactivity of the latter towards H_2SO_4 and NaOH has been briefly discussed (Beckmann and Hesse, 2009). It is noteworthy that the similar hydrolysis of $2,6\text{-}Mes_2C_6H_3SbCl_2$ under aerobic conditions produced mixed-valent arylstiboxane clusters $(2,6\text{-}Mes_2C_6H_3Sb^{V})_2(ClSb^{III})_4O_8$ and $(2,6\text{-}Mes_2C_6H_3Sb^{V})_4(ClSb^{III})_4(HOSb^{III})_2O_{14}$, which evolved from partial cleavage of Sb-C bonds (Beckmann et al., 2007). We now report that attempts at purifying $[2,6\text{-}Mes_2C_6H_3Sb(O)(OH)_2]_2$ by recrystallisation from ethanol gave rise to the partial esterification and formation of the title compound $[2,6\text{-}Mes_2C_6H_3Sb(O)(OEt)(OH)]_2$ in quantitative yield. Like the parent acid, the ester is readily soluble in organic solvents, such as $CHCl_3$, toluene, and THF. Characterization was achieved by ^1H and ^{13}C NMR spectroscopy, IR spectroscopy, microanalysis (experimental section), and X-ray crystallography. The molecular structure is shown in Figure 1. Selected bond parameters are provided in the caption of the figure. Like the parent acid, the structure of the ester comprises a centrosymmetric, four-membered Sb_2O_2 ring. The spatial arrangement of the Sb atom is distorted trigonal bipyramidal and is defined by a CO_4 donor set, whereby the atoms C10, O1, and O2 occupy the equatorial positions, whereas the atoms O1a and O3 are situated on the axial positions.

As expected for this coordination geometry, the axial Sb-O bond lengths [$Sb_1\text{-}O_{1a}$ 2.033(4) Å, Sb1-O3 1.941(5) Å] are slightly longer than the equatorial Sb-O bond lengths [Sb1-O1 1.932(4) Å, Sb1-O2 1.924(4) Å]. It is further revealed that only the axial hydroxy group of the parent acid was subject to the esterification, while the equatorial hydroxyl group remained unchanged.

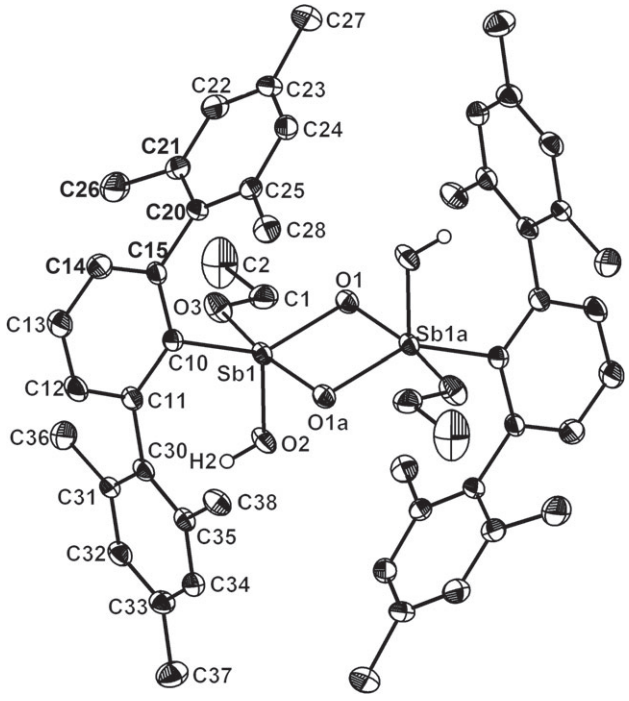

Figure 1 Molecular structure of [2,6-$Mes_2C_6H_3Sb(O)(OEt)(OH)]_2$ showing 30% probability ellipsoids and the crystallographic numbering scheme (symmetry code used to generate equivalent atoms: a=-x, -y, -z). Selected bond parameters [Å, °]: Sb1-O1 1.932(4), Sb1-O1a 2.033(4), Sb1-O2 1.924(4), Sb1-O3 1.941(5), Sb1-C10 2.156(6), O1-Sb1-O1a 78.4(2), O1-Sb1-O2 111.7(2), O1a-Sb1-O2 89.5(2), O1-Sb1-O3 92.2(2), O1a-Sb1-O3 170.0(2), O2-Sb1-O3 90.8(2), O1-Sb1-C10 133.4(2), O1a-Sb1-C10 95.3(2), O2-Sb1-C10 114.4(2), O3-Sb1-C10 93.7(2), Sb1-O1-Sb1a 101.6(2).

Table 1 Crystal data and structure refinement of [2,6-$Mes_2C_6H_3Sb(O)(OEt)(OH)]_2$.

Formula	$C_{52}H_{62}O_6Sb_2$
Formula weight (g mol^{-1})	1026.52
Crystal system	Monoclinic
Crystal size (mm)	0.27×0.25×0.23
Space group	C2/c
a, Å	19.656(2)
b, Å	13.607(1)
c, Å	17.928(2)
α, °	90
β, °	91.638(9)
γ, °	90
V, $Å^3$	4793.0(9)
Z	4
ρ_{calcd} (Mg m^{-3})	1.423
T, K	150
μ (Mo-Kα) (mm^{-1})	1.174
F(000)	2096
θ range, °	1.82–25.02
Index ranges	$-18 \le h \le 23$
	$-15 \le k \le 16$
	$-21 \le l \le 21$
Number of reflns collected	8005
Completeness to θ_{max}	96.3%
Number indep. reflns	4076
Number obsd reflns with ($I>2\sigma(I)$)	2810
Number refined params	313
GooF (F^2)	0.986
R_1 (F) ($I>2\sigma(I)$)	0.0358
wR_2 (F^2) (all data)	0.1207
$(\Delta/\sigma)_{max}$	<0.01
Largest diff peak/hole, e $Å^{-3}$	0.690/-1.204

Experimental

General

The arylstibonic acid [2,6-$Mes_2C_6H_3Sb(O)(OH)_2]_2$ was prepared according to a procedure described in the literature (Beckmann et al., 2008). The ^1H, ^{13}C, and ^{125}Te NMR spectra were recorded using Jeol GX 270 and Varian 300 Unity Plus spectrometers and are referenced to $SiMe_4$ (^1H, ^{13}C) and Me_2Te (^{125}Te). Microanalyses were obtained from a Vario EL elemental analyser.

Synthesis of [2,6-$Mes_2C_6H_3Sb(O)(OEt)(OH)]_2$

[2,6-$Mes_2C_6H_3Sb(O)(OH)_2$] (250 mg, 0.28 mmol) was dissolved in ethanol (50 mL) and was heated under reflux for 2 h. The solvent was removed in vacuum using a rotavap to give [2,6-$Mes_2C_6H_3Sb(O)(OEt)(OH)$] as a colourless microcrystalline solid (260 mg, 0.25 mmol, 98%; decomposition without melting).

^1H-NMR (C_6D_6): δ=7.50 (t, 1H; Ar), 7.11 (d, 2H; Ar), 6.95 (s, 4H; Ar), 3.25 (m, 4H; CH_2), 2.32 (s, 6H; CH_3), 1.97 (s, 12H; CH_3), 0.91 (m, 6H; CH_3). ^{13}C-NMR (C_6D_6): δ=145.4, 137.5, 137.0, 134.5, 130.3, 127.7, 108.0 (Ar), 25.2 (CH_2CH_3) 21.2 (*p*-CH_3), 20.9 (*o*-CH_3), 18.5 (CH_2CH_3). IR (KBr): $\tilde{\nu}_{OH}$=3553 cm^{-1}. Microanalysis: $C_{26}H_{31}O_3Sb$ (513.28); C 59.95 (calc. 60.84); H 6.04 (6.09)%.

X-ray crystallography

The intensity data of [2,6-$Mes_2C_6H_3Sb(O)(OEt)(OH)$] were collected on a STOE IPDS 2T area detector with graphite-monochromated Mo-Kα (0.7107 Å) radiation. Data were reduced and corrected for absorption. The structures were solved by direct methods and difference Fourier synthesis using SHELXS-97 implemented in the program WinGX 2002 (Farrugia, 1999). Full-matrix least-squares refinements on F^2 were carried out using all data. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions using a riding model. The hydrogen atom attached to O_2 was located during the last refinement cycle and was refined isotropically. Disorder

was resolved for C1 and C2 and was refined over two sites with occupancy factors of 0.5. Crystal and refinement data are listed in Table 1. Figures were created using DIAMOND (Brandenburg and Putz, 2006). Crystallographic data (excluding structure factors) for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC number 933372. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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References

Ali, S.; Baskar, V.; Muryn, C. A.; Winpenny, R. E. P. Mixed antimonate-phosphonate ligands as polydentate bridging oxygen donors. *Chem. Commun*. **2008**, 6375–6377.

Baskar, V.; Shanmugam, M.; Helliwell, M. S.; Teat, J.; Winpenny, R. E. P. Reverse-Keggin ions: polycondensation of antimonate ligands give inorganic cryptand. *J. Am. Chem. Soc*. **2007**, *129*, 3042–3043.

Beckmann, J.; Hesse, M. Reactivity of the dinuclear arylstibonic acid $[2,6\text{-}Mes_2C_6H_3Sb(O)(OH)_2]_2$ toward H_2SO_4 and NaOH. *Organometallics* **2009**, *28*, 2345–2348.

Beckmann, J.; Heek, T.; Takahashi, M. The first mixed-valent antimony(III/V) oxo clusters $(2,6\text{-}Mes_2C_6H_3Sb)_2(ClSb)_4O_8$ and $(2,6\text{-}Mes_2C_6H_3Sb)_4(ClSb)_4(HOSb)_2O_{14}$. *Organometallics* **2007**, *26*, 3633–3635.

Beckmann, J.; Finke, P.; Hesse, M.; Wettig, B. Well-defined stibonic and tellurinic acids. *Angew. Chem. Int. Ed*. **2008**, *47*, 9982–9984.

Brandenburg, K.; Putz, H. DIAMOND V3.1d. Crystal Impact GbR: Bonn, Germany, 2006.

Clark, C. J.; Nicholson, B. K.; Wright, C. E. Arylstibonic acids $[H_8(RSb)_{12}O_{28}]$; precursors to organometallic isopolyoxostibonates $[Na_2H_2(RSb)_{12}O_{30}]^-$, (R = aryl). *Chem. Commun*. **2009**, 923–925.

Farrugia, L. J. Win, G. X. suite for small-molecule single-crystal crystallography. *J. Appl. Crystalogr*. **1999**, *32*, 837–838.

Hasenbäumer, J. Über die primären Chlorstibine der aromatischen Reihe. *Ber. Dtsch. Chem. Ges*. **1898**, *31*, 2910–2914.

Jami, A. K.; Baskar, V. Tetranuclear stiboxanes $(RSb)_4O_6$, exhibiting an adamantane-type structure. *Dalton Trans*. **2012**, *41*, 12524–12529.

Jami, A. K.; Prabhu, M. S. R.; Baskar, V. Isolation of tetranuclear organoantimony oxo clusters and hexa-decanuclear polyoxostibonates. *Organometallics* **2010**, *29*, 1137–1143.

Nicholson, B. K.; Clark, C. J.; Wright, C. E.; Groutso, T. Isopolyoxometalates of antimony: arylstibonic acids $[H_8(RSb)_{12}O_{28}]$ and derived dodecanuclear polyoxostibonates $[M_2H_{10-x}(RSb)_{12}O_{30}]^{x-}$, M = Na or K. *Organometallics* **2010**, *29*, 6518–6526.

Nicholson, B. K.; Clark, C. J.; Wright, C. E.; Telfer, S. G.; Groutso, T. New Sb_{12} and Sb_{14} polyoxometalate frameworks derived from arylstibonic acids: $[LiH_3(p\text{-}MC_6H_4Sb)_{12}O_{28}]^{4-}$ and $[BaH_{10}(p\text{-}MeC_6H_4Sb)_{12}O_{34}]$. *Organometallics* **2011**, *30*, 6612–6616.

Nicholson, B. K.; Clark, C. J.; Telfer, S. G.; Groutso, T. Isopolyoxometalates derived from arylstibonic acids with "reverse-Keggin ion" structures based on $[M(RSb)_{12}O_{28}]$ cores, M = Co(II) or Zn(II). *Dalton Trans*. **2012**, *41*, 9964–9970.

Piedra-Garza, L. F.; Diekman, M. H.; Moldovan, O.; Breunig, H. J.; Kortz, U. Organoantimony-containing polyoxometalate: $[\{PhSbOH\}_3(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{9-}$. *Inorg. Chem*. **2009**, *48*, 411–413.

Prabhu, M. S. R.; Jami, A. K.; Baskar, V. Organoantimony(V) oxido cubane cluster $[(p\text{-}X\text{-}C_6H_4Sb)_4(O)_4(Ph_2SiO_2)_4]$ (X = Cl, Br) stabilized by diphenyldisiloxides. *Organometallics* **2009**, *28*, 3953–3956.