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Antimony Amide Oxide and Antimony Chloride Oxide Wrapped in an Organoaluminum Framework

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Syntheses of trimetallic aluminum and antimony compounds containing an Al_2O_2SbN and an Al_2O_2SbCl core in [LAl(Me)(μ-O)]$_2$Sb(NMe$_2$) and [LAl(Me)(μ-O)]$_2$SbCl, respectively, are reported. The former compound represents an example of an amide oxide of antimony and the latter is an example of a chloride oxide of antimony incorporated in an organoaluminum framework which in turn is supported by a sterically encumbered β-diketiminate ligand L {L = HC[C(Me)N-2,6-iPr$_2$C$_6$H$_3$]$_2$}. The solid-state structure of [LAl(Me)(μ-O)]$_2$Sb(NMe$_2$) was elucidated by the aid of single-crystal X-ray diffraction technique which shows the molecule to crystallize in the triclinic space group $P\bar{1}$.

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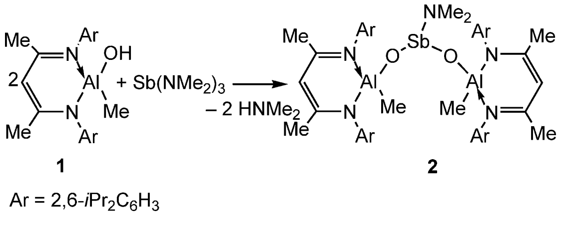
Introduction

Antimony exists in nature as sulfide minerals stibnite (Sb_2S_3), ullmanite (NiSbS), livingstonite ($HgSb_4S_8$), jamesonite ($FePb_4Sb_6S_{14}$) etc. Small amounts of oxide minerals are also known, e.g. valentinite (Sb_2O_3), cervantite (Sb_2O_4) and stibiconite ($Sb_2O_4\cdot H_2O$), formed by weathering.[1] Apart from the oxide minerals, the mixed amide oxide and halide oxide compounds of Sb are extremely rare. SbOCl can be obtained by treatment of $SbCl_3$ with a limited amount of H_2O. However, no mineral of antimony containing an oxygen and nitrogen environment around the Sb atom is known. Syntheses of antimony compounds with varied amounts of oxygen, nitrogen, and (or) chlorine per equivalent of antimony compared to those observed in naturally occurring minerals is a challenging task. This would involve the incorporation of other substituents (preferably metal atoms) on these atoms (O and N) in order to satisfy their valency. Our recent resurgence in the area of organoaluminum hydroxides and their utilization as ligands has afforded useful compounds with Al–O–M units.[2–13] Further elaboration of this work has now resulted in mixed-metal Al/Sb compounds. Only two oxygen-bridged organometallic compounds have been reported which contain Al and Sb atoms. The first compound is an ionic aluminosilsesquioxane with the cation Me_4Sb^+, without showing any formal Al–O–Sb bond;[14] only the second compound contains an Al–O–Sb unit in an aluminum/antimony heterodinuclear porphyrin [(oep)(Me)(Sb–O–Al)(oep)]ClO$_4$ (oep = octaethylporphyrinate), synthesized by the very sluggish reaction of [(oep)(Me)Sb(OH)]ClO$_4$ with (oep)AlMe in only 7% yield.[15] However, neither of these have been structurally characterized. To the best of our knowledge there have been no reports on the syntheses of antimony oxide derivatives containing amide or halide groups.

Herein, we report on the syntheses and structural characterization of [LAl(Me)(μ-O)]$_2$Sb(NMe$_2$) (**2**) and [LAl(Me)(μ-O)]$_2$SbCl (**4**) {L = HC[C(Me)N-2,6-iPr$_2$C$_6$H$_3$]$_2$}. Compounds **2** and **4** represent the first examples of antimony amide oxide and antimony chloride oxide which are surrounded by an organoaluminum framework.

Results and Discussion

The reaction of the aluminum hydroxide[2,3] LAl(Me)OH (**1**) with the homoleptic dimethylamide of antimony,[16] Sb(NMe$_2$)$_3$, in a stoichiometric ratio of 2:1 leads to the formation of [LAl(Me)(μ-O)]$_2$Sb(NMe$_2$) (**2**) (Scheme 1). The reaction proceeds with the elimination of HNMe$_2$ with concomitant formation of Al–O–Sb bonds. Surprisingly, attempts to replace the remaining dimethylamide moiety on the antimony atom, when Sb(NMe$_2$)$_3$ was treated with 3 equiv. of **1**, were not successful. Only **2** and unreacted **1**



Scheme 1. Synthesis of antimony amide oxide compound **2**.

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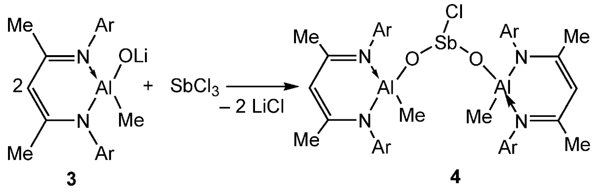
were detected in the reaction mixture. It is possible that the steric demand of the β-diketiminate ligand on the aluminum atoms which are surrounding the Sb atom in **2** do not allow the formation of the trisubstituted antimony product.

Similar results have been obtained in the reaction of the lithium derivative of **1**, $[LAl(Me)OLi]_3$ (**3**)[17] with $SbCl_3$ in a 3:1 stoichiometric ratio to yield only $[LAl(Me)(\mu\text{-}O)]_2SbCl$ (**4**) and unreacted **3**. Formation of **4** as the sole reaction product has been optimized as shown in Scheme 2. Compounds **2** and **4** are air- and moisture-sensitive, colorless crystalline solids and melt with decomposition at 160 and 130 °C, respectively. The EI mass spectrum of **2** reveals peaks that can be assigned only to the ligand and its fragments. However, in the case of **4** an ion peak at *m*/*z* = 1093 was observed as the base peak corresponding to $[M^+ - Me]$, and the fragment at *m*/*z* = 1073 corresponds to $[M^+ - Cl]$.



3

Ar = 2,6-$iPr_2C_6H_3$

4

Scheme 2. Preparation of antimony chloride oxide compound **4**.

The ^{1}H NMR spectrum of **2** shows that two halves of the molecule resonate at slightly different frequencies. The Al–*Me* resonances are observed at δ = –0.57 and –0.34 ppm which are slightly downfield-shifted compared to that observed in **1** (δ = –0.95 ppm) (Figure 1).[2,3] The $SbNMe_2$ protons resonate at δ = 2.51 ppm. The Al–*Me* resonance in the case of **4** were observed at δ = –0.63 and –0.56 ppm and are downfield-shifted to that of **1**.[2,3] Single crystals of **2** suitable for X-ray analysis were obtained from an *n*-hexane solution. Compound **2** crystallizes in the triclinic system with the space group $P\bar{1}$.[18] The $SbNMe_2$ moiety is disordered over two positions with an occupancy ratio of 0.974:0.026; only the major orientation will be discussed in the text. Table 1 lists selected metric parameters of **2** and Table 2 depicts the crystallographic data of **2**. The solid-state structure of **2** supports the initial indication from the ^{1}H NMR findings that the two halves of the molecule are not symmetry-related. The geometry around the central Sb(1) atom is distorted trigonal, where the substituents are not arranged in a plane. The AlMe groups are *trans* with respect to each other while the NMe_2 group on the Sb(1) atom is *trans* to the Al–C(60) and *cis* to the Al–C(30) groups.

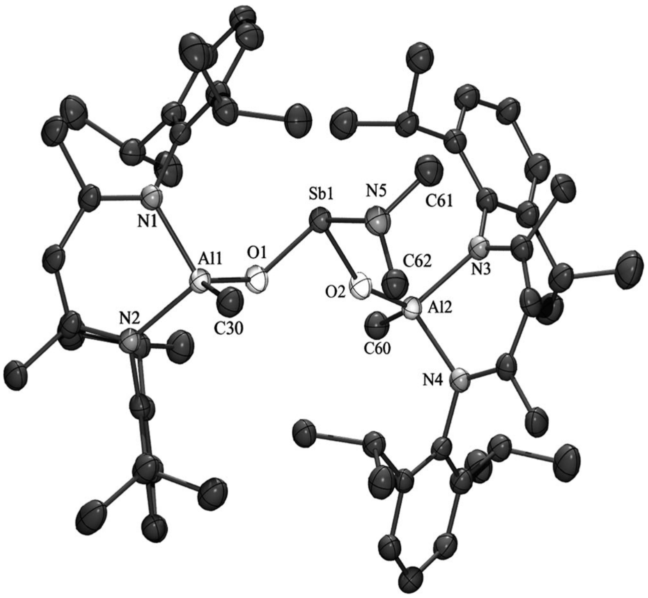


Figure 1. Molecular crystal structure of $[LAl(Me)(\mu\text{-}O)]_2Sb(NMe_2)$ (**2**). Thermal ellipsoids are shown with 50% probability. The hydrogen atoms of the C–H bonds are omitted for clarity.

Table 1. Selected metric parameters of **2**. Only the bonds involving the 97% conformer are listed.

Bond lengths [Å]		Bond angles [°]	
Al(1)–O(1)	1.709(2)	O(1)–Sb(1)–O(2)	96.0(1)
Al(2)–O(2)	1.713(2)	C(30)–Al(1)–O(1)	117.3(1)
Sb(1)–O(1)	1.925(2)	C(60)–Al(2)–O(2)	116.4(1)
Sb(1)–O(2)	1.928(2)	O(1)–Sb(1)–N(5)	96.0(1)
Sb(1)–N(5)	2.017(3)	O(2)–Sb(1)–N(5)	100.6(1)
Al(1)–C(30)	1.965(3)	Al(1)–O(1)–Sb(1)	138.9(1)
Al(2)–C(60)	1.953(3)	Al(2)–O(2)–Sb(1)	151.8(1)

Table 2. Crystallographic data for the structural analysis of compound **2**.

	$[LAl(Me)(\mu\text{-}O)]_2SbNMe_2$ (**2**)
Empirical formula	$C_{62}H_{94}Al_2N_5O_2Sb$
Formula mass	1117.13
T [K]	100(2)
Crystal system	triclinic
Space group	$P\bar{1}$
a [Å]	13.402(1)
b [Å]	16.104(2)
c [Å]	16.760(2)
α [°]	95.05(2)
β [°]	103.26(3)
γ [°]	114.43(2)
V [Å^3]	3137(1)
Z	2
D(calcd.) [g cm^{-3}]	1.183
μ(Cu-K_α) [mm^{-1}]	4.084
F(000)	1188
θ range [°]	2.77–59.05
Index range	$-14 \le h \le 14$ $-17 \le k \le 17$ $-18 \le l \le 18$
Reflections collected	23938
Independent reflections	8562
Data/restraints/parameters	85629/288/716
$R1$, $wR2$ [$I > 2\sigma(I)$][a]	0.0321, 0.0766
$R1$, $wR2$ (all data)[a]	0.0353, 0.0790
GOF	1.048
$\Delta\rho$(min), $\Delta\rho$(max) [e·Å^{-3}]	0.870, –0.710

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.

The terminal aluminum atoms in **2** form highly distorted tetrahedra, and the Sb atom resides in a bent conformation of the O(1)–Sb(1)–O(2) framework with a bond angle of

96.0(1)°. The Sb(1)–N(5) bond length is 2.017(3) Å, whereas the Sb–O bond lengths are 1.928(2) and 1.925(2) Å (av. 1.926 Å), which are shorter than that observed in the inorganic cluster $CaCu_3Cr_2Sb_2O_{12}$ [Sb–O 2.048(6) Å].[19] The Al(1)–O(1) [1.709(2) Å] and Al(2)–O(2) [1.713(2) Å] bonds are slightly shorter than that of LAl(Me)OH (**1**) [1.731(3) Å].

Conclusion

We have shown facile syntheses of trinuclear oxides containing aluminum and antimony. These procedures utilize the reactions of an Al–OH motif and an Al–OLi unit and allow to control the replacement of amide or halide groups present on the Sb atom. Thus, the resultant compounds $[LAl(Me)(\mu\text{-}O)]_2Sb(NMe_2)$ and $[LAl(Me)(\mu\text{-}O)]_2Sb(Cl)$ are novel heterotrinuclear oxides containing reactive amide and chloride groups. These groups on the central antimony atom should allow further elaboration of these trinuclear derivatives into aggregates with higher nuclearity.

Experimental Section

$[LAl(Me)(\mu\text{-}O)]_2Sb(NMe_2)$ (2): To a solution of $Sb(NMe_2)_3$ (0.25 g, 1.00 mmol) in toluene (15 mL), a solution of LAl(Me)OH (0.95 g, 2.00 mmol) in toluene (25 mL) was added drop by drop at 0 °C. The solution was warmed to room temperature and stirred overnight. After removal of all volatiles, the product was extracted with *n*-hexane (40 mL). Yield 0.67 g, 60%. M.p. 160 °C (decomp.). $C_{62}H_{94}Al_2N_5O_2Sb$ (1117.17): calcd. C 66.66, H 8.48, N 6.27; found C 66.73, H 8.62, N 6.30. Only peaks of the ligand and its fragments were observed under mass-spectrometric conditions. ^1H NMR (200 MHz, C_6D_6): δ = –0.57 (s, 3 H, Al*Me*), –0.34 (s, 3 H, Al*Me*), 1.14 (m, 24 H, CH*Me*$_2$), 1.36 (2 overlapped d, $^3J_{HH}$ = 6.8 Hz, 18 H, CH*Me*$_2$), 1.49 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, CH*Me*$_2$), 1.53 (s, 3 H, C*Me*), 1.56 (s, 9 H, C*Me*), 2.51 (s, 6 H, SbN*Me*$_2$), 3.30 (2 overlapped sept, 4 H, C*H*Me$_2$), 3.62 (2 overlapped sept, $^3J_{H\text{-}H}$ = 6.8 Hz, 4 H, C*H*Me$_2$), 4.86 (s, 1 H, γ-C*H*), 4.95 (s, 1 H, γ-C*H*), 7.14–7.10 (m, 12 H, *Ar*) ppm.

$[LAl(Me)(\mu\text{-}O)]_2SbCl$ (4): To a solution of $SbCl_3$ (0.23 g, 1.00 mmol) in toluene (10 mL) was added a solution of LAl(Me)-OLi (0.96 g, 2.00 mmol) in toluene (20 mL) at 0 °C. The mixture was stirred at room temperature overnight. After removal of all volatiles in vacuo, the title compound was extracted with *n*-pentane (10 mL). Yield 0.38 g, 34%. M.p. 130 °C (decomp.). $C_{60}H_{88}Al_2ClN_4O_2Sb$ (1108.54): calcd. C 65.01, H 8.00, N 5.05; found C 65.11, H 8.08, N 5.10. EI-MS: *m/z* (%) = 1093 (100) [M^+ – Me], 1073 (5) [M^+ – Cl]. ^1H NMR (200 MHz, C_6D_6): δ = –0.63 (s, 3 H, Al*Me*), –0.56 (s, 3 H, Al*Me*), 1.03 (d, $^3J_{HH}$ = 6.4 Hz, 12 H, CH*Me*$_2$), 1.26 (2 overlapped d, $^3J_{HH}$ = 7.0 Hz, 24 H, CH*Me*$_2$), 1.48 (d, $^3J_{HH}$ = 6.4 Hz, 12 H, CH*Me*$_2$), 1.55 (s, 12 H, C*Me*), 3.21 (sept, $^3J_{HH}$ = 6.4 Hz, 4 H, C*H*Me$_2$), 3.79 (sept, $^3J_{HH}$ = 6.4 Hz, 4 H, C*H*Me$_2$), 4.99 (s, 1 H, γ-C*H*), 5.06 (s, 1 H, γ-C*H*), 7.03–7.13 (m, 12 H, *Ar*) ppm.

X-ray Structure Determination of 2: A suitable crystal of **2** was mounted on a glass fiber and coated with paraffin oil. Data for **2** was obtained with a Bruker three-circle diffractometer equipped with a SMART 6000 CCD detector using mirror-monochromated Cu-K_α radiation (λ = 1.54178 Å). The structure was solved by direct methods using SHELXS-97[20] and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[21] All non-hydrogen atoms were refined anisotropically. Atom scattering factors (including anomalous scattering) were taken from the "International Tables for X-ray Crystallography".[18] Hydrogen atoms connected to carbon atoms were included at geometrically calculated positions and refined using a riding model. CCDC-665790 (**2**) contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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