

Some bimetallic alkoxides and phenoxides of antimony(V) [MSb(OR)₆]

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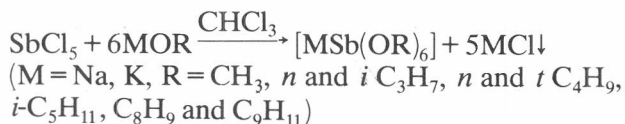
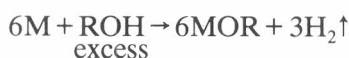
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Bimetallic alkoxides and phenoxides of the type [MSb(OR)₆] (M = Li, Na, K, R = CH₃, *n* and *i*-C₃H₇, *n* and *t*-C₄H₉, *i*-C₅H₁₁, 2,6-dimethylphenol, 2,3,6-trimethylphenol) have been prepared by the reaction of SbCl₅ with MOR in 1:6 molar ratio in chloroform. The IR, ¹H and ¹³C NMR spectral studies of these monomeric, moisture-sensitive, non-volatile and non-conducting bimetallic alkoxides/phenoxides have been reported.

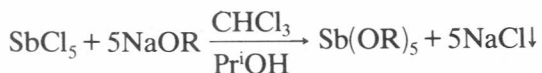
The formation of two bimetallic alkoxides of antimony(V) of the type [NaSb(OR)₆] (R = CH₃, C₂H₅) has been reported during the titration of sodium and antimony(V) alkoxides in parent alcohols¹. Considered initially as "alkoxosalts", no attempt appears to have been made to isolate such derivatives and explore their chemistry. We report herein the synthesis and properties of some bimetallic alkoxides/phenoxides of antimony(V) of the type [MSb(OR)₆] depicting covalent characteristics.

Materials and Methods

Bimetallic alkoxides and phenoxides of the type [MSb(OR)₆] were prepared by the direct reaction of antimony(V) chloride (in CHCl₃) with alkali metal alkoxides/phenoxides in 1:6 molar ratio at ~ 0°C and under completely anhydrous conditions:



In view of the solubility of LiCl in organic solvents, LiSb(OR)₆ could be synthesised by the reactions of Sb(OR)₅ (prepared *in situ* by the reaction of SbCl₅ with NaOR in 1:5 molar ratio) with LiOR:



For the sake of brevity, details are given only for two compounds with analytical data, etc. for other illustrative derivatives in Table 1.

Synthesis of [KSb(OPr^{*i*})₆]

A solution of potassium metal (2.45 g, 62.82

mmole) in isopropanol (20 ml) was added to an ice-cold solution of SbCl₅ (3.12 g, 10.43 mmole) in CHCl₃ (~ 15 ml). An exothermic reaction took place immediately. The contents were refluxed for 4 hr under dry nitrogen atmosphere, cooled, KCl formed was filtered off and the filtrate concentrated under reduced pressure to yield a brown viscous liquid (96% yield).

Synthesis of [LiSb(OPr^{*i*})₆]

A clear solution of sodium (1.05 g, 45.65 mmole) in isopropanol (25 ml) was added to an ice-cold solution of SbCl₅ (2.72 g, 9.09 mmole) in CHCl₃ (15 ml). An exothermic reaction took place immediately. The contents were refluxed for 1 hr under dry nitrogen atmosphere and to this was added a solution of Li (0.063 g, 9.09 mmole) in isopropanol (~ 10 ml) and the contents were again refluxed for 1 hr. After cooling, NaCl formed was filtered off and the filtrate concentrated under reduced pressure to furnish a yellow solid (85% yield).

Analytical measurements

Molecular weights were determined in parent alcohols or benzene with the help of a Gallenkamp ebulliometer equipped with a thermistor sensor. Molar conductances were measured with the help of a Sytronic conductivity bridge using a specially fabricated conductivity cell (cell constant 0.22). Infrared spectra of the compounds were recorded on a Perkin-Elmer 577 spectrophotometer, and ¹H and ¹³C NMR spectra on a FX 90Q machine. Detailed analysis of organic component of the derivatives could be carried out only in a few cases, as the C/H equipment tended to get choked (maybe due to Sb₂O₅) during the analysis. For the characterization of these derivatives, special attention was paid to the molecular weight determination and antimony percentage along with spectroscopic data.

Table 1—Bimetallic Alkoxides and Phenoxides of Antimony [MSb(OR)₆]

Reactants gm (mmole)		Molar ratio	Compound (yield %)	Nature	Mol wt found (calc.)	Found (Calc.) (%)			
SbCl ₅	Li/Na/K					Sb	Alkoxy	C	H
1.49 (4.98)	1.18 (50.26)	1:6	[KSb(OMe) ₆] (82)	White solid	372 MeOH (347)	35.37 (35.11)	—	20.08 (20.74)	4.74 (5.19)
3.12 (10.43)	2.45 (62.82)	1:6	[KSb(OPr ⁱ) ₆] (96)	Brown viscous liquid	531 Pr ⁱ OH (515)	22.47 (23.65)	67.87 (68.77)	40.99 (41.95)	7.76 (8.16)
3.03 (10.12)	1.38 (60.00)	1:6	[NaSb(OPr ⁱ) ₆] (90)	Brown solid	—	23.62 (24.41)	70.55 (70.98)	41.50 (43.30)	8.88 (8.42)
3.79 (9.09)	0.063 (9.08)	1:1	[LiSb(OPr ⁱ) ₆] (85)	Brown needle crystal	506 Pr ⁱ OH (483)	24.96 (25.22)	73.91 (73.34)	44.02 (44.74)	7.96 (8.70)
2.52 (8.42)	8.22 (51.37)	1:6	[KSb(O-2, 6-DMP) ₆] (90)	Brown sticky solid	990 C ₆ H ₆ (971)	11.97 (12.54)	—	64.21 (64.96)	5.27 (6.09)
1.26 (4.21)	4.48 (25.60)	1:6	[KSb(O-2,3,6-TMP) ₆] (94)	Brown sticky solid	895 C ₆ H ₆ (887)	13.32 (13.73)	—	66.18 (66.75)	6.13 (6.79)
2.74 (9.16)	2.16 (55.38)	1:6	[KSb(OPr ⁿ) ₆] (84)	Brown viscous liquid	499 Pr ⁿ OH (515)	23.00 (23.65)	—	—	—
2.23 (7.45)	1.73 (44.36)	1:6	[KSb(OBu) ₆] (94)	Brown viscous liquid	611 C ₆ H ₆ (599)	19.79 (20.33)	—	—	—
1.41 (4.71)	1.09 (27.95)	1:6	[KSb(OBu ^t) ₆] (94)	Brown viscous liquid	—	19.81 (20.33)	—	—	—
1.63 (5.45)	1.27 (32.56)	1:6	[KSb(OAm ¹) ₆] (84)	Brown viscous liquid	706 C ₆ H ₆ (683)	17.19 (17.83)	—	—	—

[O-2, 6-MP= 2, 6-Dimethylphenol, O-2,3,6-TMP= 2,3,6-trimethylphenol]

Results and Discussion

Some of these bimetallic alkoxides/phenoxides are coloured solids, which could be purified by recrystallisation from parent alcohols. The characterisation data are presented in Table 1. The other alkoxides are either viscous liquids or sticky solids. All these are soluble in parent alcohols and sparingly soluble in other organic solvents. They are monomeric in refluxing parent alcohols and are thermally unstable even under reduced pressure. The high solubilities and low values of molar conductances of these alkoxides in parent alcohols suggest that they are essentially covalent compounds. Monomeric nature of these bimetallic alkoxides could be due to antimony acquiring a higher coordination number through intramolecular dative bondings of alkoxy groups. Although corroborated by their monomeric and nonconducting nature, the presence of bridging alkoxy groups could not be confirmed by NMR spectra in view of their fast exchange even at lower temperatures.

Various bands in the IR spectra of [MSb(OR)₆] have been assigned by comparison with those of simple alkoxides of Sb(III)² and chloro-derivatives of Sb(V)³⁻⁶. The broad bands in the regions 1240-1145, 1080-1020 cm⁻¹ and 980-920 cm⁻¹, have been as-

signed to OR (R = alkyl)⁷⁻¹¹, terminal νSbO - C and bridging νSbO - C respectively. The bands observed in the regions 640-580 and 570-530 cm⁻¹ have been assigned to ν_sSb - OC and ν_{as} Sb - OC bonds and those in the regions of 440-385, and 340-285 cm⁻¹, to Sb - OC symmetric and antisymmetric bending vibrations respectively².

In the bimetallic phenoxides of antimony(V), the νC = C mode occurs in the region 1580-1550 cm⁻¹. The νSbO - C (terminal and bridging) modes have also been assigned to bands occurring in the regions 1080-1060 and 975-970 cm⁻¹ respectively. ν_s SbO - C and ν_{as} SbO - C modes occur in the regions 640-580 and 575-560 cm⁻¹ respectively. The symmetric and antisymmetric bending vibrations of νSbO - C modes lies in regions 400-385 and 310-285 cm⁻¹ respectively.

The ¹H NMR data of bimetallic alkoxides of antimony(V) have been compared with those of free alcohols¹². The ¹H NMR spectra of bimetallic alkoxides display downfield chemical shift as compared to those observed in the free alcohols (Table 2). The integration ratio corresponds to the number of chemically different types of protons present in the bimetallic alkoxides/phenoxides of antimony(V) (Table 2).

Table 2— ^1H and ^{13}C NMR Spectral Data of $[\text{MSb}(\text{OR})_6]$ (Spectral of compounds at sl nos 1-8 and 10 were recorded in CDCl_3 , while that of 10 in CCl_4)

Sl No	Compound	Nuclei	CH_3	$-\text{CH}_2-$	$-\text{CH}_2-$	$-\text{CH}_2\text{O}$	$-\text{CHO}$	$-\text{CH}$	Aromatic
1	$[\text{KSb}(\text{OMe})_6]$	^1H	3.35(s)						
		^{13}C	58.24						
2	$[\text{LiSb}(\text{OPr}^i)_6]$	^1H	1.11(br)				3.26(h)		
		^{13}C	25.46				59.30		
3	$[\text{NaSb}(\text{OPr}^i)_6]$	^1H	1.23(d)				4.06(H)		
		^{13}C	25.25				64.25		
4	$[\text{KSb}(\text{OPr}^i)_6]$	^1H	1.22(d)				4.07(h)		
		^{13}C	25.31				63.33		
5	$[\text{KSb}(\text{OPr}^n)_6]$	^1H	0.97(t)	1.69(h)	—	3.78(t)			
		^{13}C	22.59	40.58	—	62.08			
6	$[\text{KSb}(\text{OBu})_6]$	^1H	0.97(t)	1.52(m)	1.52(m)	3.69(t)			
		^{13}C	13.82	19.35	31.86	64.20			
7	$[\text{KSb}(\text{OBu}^t)_6]$	^1H	1.30(s)						
		^{13}C	29.63						
8	$[\text{KSb}(\text{OAm}^i)_6]$	^1H	0.93(d)	1.57(m)	—	4.09(br)	—	1.57(m)	
		^{13}C	22.38	40.53	—	61.76	—	24.54	
9	$[\text{KSb}(\text{O}-2, 6\text{-DMP})_6]$	^1H	2.26(s)						6.85(m)
		^{13}C							7.02(d)
10	$[\text{KSb}(\text{O}-2,3,6\text{-TMP})_6]$	^1H	2.17(br)						6.48(d)
		^{13}C							6.70(d)

[s = singlet d = doublet t = triplet h = heptat m = multiplet br = broad

When the positions of these signals are compared with those of the corresponding bimetallic alkoxides of antimony (III), e.g. $[\text{KSb}(\text{OR})_4]$, no significant change is observed. The presence of only one type of ^1H NMR signal indicates the possibility of fast exchange of terminal and bridging alkoxy groups in the NMR time scale.

Similarly, ^{13}C NMR spectral data show the presence of the expected number of signals corresponding to number of chemically different types of carbon atoms present in these bimetallic alkoxides. The ^{13}C NMR data are summarized in Table 2. Downfield chemical shifts of ^{13}C nuclei in bimetallic alkoxides have been observed as compared to those of the free alcohols¹². However, in comparison to the corresponding bimetallic alkoxides of antimony(III), no significant change in the chemical shifts of ^{13}C nuclei has been observed.

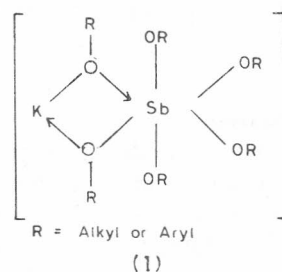
On the basis of the above studies, an octahedral structure (I) may be proposed for these bimetallic alkoxides/phenoxides of antimony(V):

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