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Reactions of Sb(V) chloride with crown ethers: formation of hydronium ion–crown ether antimon(V)ate salts

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Abstract

The hydronium ion–crown ether antimon(V)ate salts [(H_3O)(18-crown-6)][$SbCl_6$], [(H_3O)(12-crown-4)$_2$][$SbCl_6$] and [(H_3O)(15-crown-5)][$SbCl_6$] have been isolated from the reactions of $SbCl_5$ and the appropriate crown ether in acetonitrile solution. Identification of these salts follows from microanalytical, IR, Vis–UV, ^{1}H and ^{121}Sb NMR data. In one case, viz. $SbCl_5$/15-crown-5/MeCN antimon(V)ate salt formation is accompanied by redox formation ((Sb(V) → Sb(III)) of the neutral complex $SbCl_3$·15-crown-5. Aspects of the possible routes leading to antimon(v)ate salt and/or redox formation are discussed.

Introduction

The ability of crown ethers to bind cations, anions or neutral species has aroused much interest in terms of both bonding and structural considerations [1]. The structural characterisation by Nicholson and co-workers [2] of $SbCl_3$·15-crown-5, in which a pyramidal $SbCl_3$ unit is symmetrically bonded to the five oxygen atoms of the ring, signalled the first example of complex formation involving a tervalent Group VB halide (M = As, Sb, Bi). Other such complexes featuring a similar regular 'half-sandwich' structure now include: $AsCl_3$·12-crown-4 [3], $AsCl_3$·15-crown-5 [3], $SbCl_3$·18-crown-6·MeCN [4], $BiCl_3$·15-crown-5 [3, 5], $BiCl_3$·18-crown-6 [6], $BiCl_3$·12-crown-4 [7], $SbCl_3$·12-crown-4 [3]. As exceptions, 2$BiCl_3$·18-crown-6 [7] has an ionic formulation 2[$BiCl_2$·18-crown-6]$^+$[Bi_2Cl_8]$^{2-}$ wherein the bismuth cation is eight coordinate (bicapped trigonal prismatic geometry) and $BiCl_3$·18-crown-6·H_2O [6] has the solvated $BiCl_3$ unit in an edge location directly bonded to only three of the oxygen atoms of the crown ether, i.e. seven-coordinate metal geometry. For all these compounds the lone pair associated with M(III) appears to be stereochemically active.

In this paper we describe the reactions of the pentavalent halide $SbCl_5$ and the crown ethers 12-crown-4, 15-crown-5 and 18-crown-6 which have revealed a quite unexpected pattern of hydronium ion (H_3O^+)–crown ether antimon(V)ate salt formation.

Experimental

All operations were carried out under a nitrogen atmosphere. $SbCl_5$ and the crown ether ligands were used directly as supplied commercially. Benzene, hexane and acetonitrile were stored over calcium hydride and freshly distilled prior to use. IR spectra were recorded as mulls (CsI plates) using a Perkin-Elmer 580B spectrometer. ^{121}Sb NMR spectra (95.72 MHz) were recorded on a Bruker WH 400 spectrometer and ^{1}H NMR spectra (200 MHz) were recorded on a Perkin-Elmer R34 spectrometer. Electronic spectra were recorded on a Shimadzu UV 35 spectrophotometer using MeCN solutions sealed in quartz cells. Elemental analyses were performed by Medac Ltd., Brunel University, Uxbridge, Middlesex. Chloride was determined by the Volhard titration.

Preparation of the complexes

(a) [(H_3O)(18-crown-6)][$SbCl_6$] (I)

18-crown-6 (2.93 g, 11.1 mmol) in acetonitrile (20 cm^3) was added dropwise to a cooled (−20 °C), stirred solution of $SbCl_5$ (3.32 g, 11.1 mmol) in acetonitrile (50 cm^3) under a nitrogen atmosphere. The yellow solution initially formed changed to a deep red colour on warming to room temperature. This solution was stirred for

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24 h. Removal of solvent provided a brown–red tacky solid which was thoroughly washed with hexane (6 × 20 cm^3). Repeated extraction of this material using boiling acetonitrile and activated charcoal finally gave a light yellow solution from which colourless chunky crystals of **I** were obtained (1.33 g, 19.4% based on $SbCl_5$).

(b) $[(H_3O)(12\text{-crown-4})_2][SbCl_6]$ (II)

Following the procedure as in (a) above, the reaction of 12-crown-4 (2.18 g, 12.4 mmol) and $SbCl_5$ (3.68 g, 12.3 mmol) in acetonitrile provided colourless needle crystals of **II** (1.96 g, 22.6% based on $SbCl_5$).

(c) $SbCl_3{\cdot}15\text{-crown-5}$ (III) and
$[(H_3O)(15\text{-crown-5})][SbCl_6]$ (IV)

Following the procedure as in (a) above, the reaction of 15-crown-5 (1.66 g, 7.6 mmol) and $SbCl_5$ (2.26 g, 7.5 mmol) in acetonitrile provided a matte of colourless crystals in which small quantities of pale yellow cubic crystals are interspersed. Physical separation by careful manipulation under a microscope provided **III** (0.45 g, 13.3% based on $SbCl_5$) and **IV** (0.04 g, 1.1% based on $SbCl_5$).

Results and discussion

Direct addition of the crown ethers (12-crown-4, 15-crown-5, 18-crown-6) to $SbCl_5$ in acetonitrile at −20 °C under a dinitrogen atmosphere provides characteristic yellow solutions which rapidly assume a deep red colour on warming to room temperature. The products obtained from these separate reactions following conventional work-up and final extraction with boiling acetonitrile/activated charcoal, are listed in Table 1.

(a) Reaction with 18-crown-6

The resulting faint yellow solution provided colourless chunky crystals of the hydronium–crown ether (1:1) complex $[(H_3O)(18\text{-crown-6})][SbCl_6]$ (**I**) as identified by spectroscopic and analytical data (Table 1). Typically the IR spectrum shows ligand $\rho(CH_2)$ rocking, 970 cm^{-1}, ν(C–C) stretching, 839 cm^{-1} bands and splitting of the ν(C–O–C) stretching band (1110 cm^{-1}) into a doublet of 1141, 1094 cm^{-1} following complexation; the dominant band in the far IR region ν(Sb–Cl) 338 cm^{-1} is characteristic for $SbCl_6^-$ [8]. An intense charge transfer band, λ_{max} 37 023 cm^{-1} in the Vis–UV spectrum and a clearly resolved singlet (δ −0.10 ppm) in the ^{121}Sb NMR spectrum also identifies the $SbCl_6^-$ anion [9, 10]. The ^{1}H NMR spectrum shows a singlet δ3.67 for the crown protons, cf. free ligand δ3.51, and a weak signal at δ10.1 assigned to the hydronium ion.

In 1972 Izatt *et al.* [11] first postulated hydronium ion encapsulation by a crown ether for the complexes $[(H_3O)$(dicyclohexyl 18-crown-6)[X] (X = ClO_4, PF_6) on the evidence of IR spectroscopic data. Confirmation that a hydronium cation had been anchored into the crown cavity came some ten years later with the X-ray crystal structure determination by Behr *et al.* [12] of $[(H_3O)$(tetracarboxylic 18-crown-6)](Cl]. The list of complexes featuring hydronium ion encapsulation by 18-crown-6 (and substituted derivatives) now includes: $[(H_3O)(18\text{-crown-6})][Y]$ Y = PF_6, ClO_4, BF_4, I, Br_3 [13]; $[(H_3O)(18\text{-crown-6})]_2[Mo_6O_{19}]$ [14]; $[(H_3O)$(dicyclohexyl 18-crown-6)$]_2[Th(NO_3)_6]$ [15]; $[(H_3O)(18\text{-crown-6})][HCl_2]$ [16] and the related $[HBr_2]$ salt [17]; $[(H_3O)$(dicyclohexyl 18-crown-6)$]_2[UO_2Cl_4]{\cdot}2C_6H_6$ [18]; $[(H_3O)$(dicyclohexyl 18-crown-6)$]_2[UCl_6]$ [18]; $[(H_3O)(18\text{-crown-6})]_2[Pd_2Cl_6]$ [19]; $[(H_3O)(18\text{-crown-6})]_2[MCl_4]$, M = Zn, Mn [20]. In all cases the H_3O cation is located in the crown cavity by three strong $OH^+ \cdots O$ hydrogen bonds involving alternate oxygen atoms of the crown ring with the possibility of further stabilisation from ion–dipole interactions. Subtle variations in the separation distance $O_{cation} \cdots O_{ring}$ (mean plane of the six oxygen atoms) have been discussed in relation to the geometry (pyramidal *v* planar) adopted by the H_3O^+ cation. Formation of a similar complex in the present instance is viewed as an off-shoot of limited hydrolysis of $SbCl_5$ (see discussion below). With so many examples at hand, structural parameters of **I** are not being pursued.

(b) Reaction with 12-crown-4

Here the resulting faint yellow solution provided colourless needle crystals of the hydronium ion–crown ether (1:2) complex $[(H_3O)(12\text{-crown-4})_2][SbCl_6]$ (**II**) as identified by spectroscopic and analytical data (Table 1). Again an intense band ν(Sb–Cl) 338 cm^{-1} in the far IR spectrum, an intense charge transfer band λ_{max} 37 901 cm^{-1} in the UV spectrum and a clearly resolved singlet δ −0.12 ppm in the ^{121}Sb NMR spectrum denote the presence of $SbCl_6^-$ anions. No significant changes are observed in the IR band profile of the ligand (1500–800)cm^{-1}. The ^{1}H NMR spectrum exhibits a sharp singlet for the crown ($-CH_2-$) protons δ3.63 (uncomplexed δ3.58) but we were unable to locate the protons of the hydronium cation. Limited solubility and/or H/D exchange between H_3O^+ and CD_3CN are possible factors here.

Only one example of hydronium ion encapsulation by 12-crown-4 has been reported previously: addition of concentrated aqueous HPF_6 to the crown dissolved in CH_2Cl_2 afforded $[(H_3O)(12\text{-crown-4})_2][PF_6]$ [13]. A sandwich structure for

TABLE 1. Microanalytical and principal spectroscopic data for crown ether complexes

Compound	Anal. found (calc.) (%)			Infrared[a] (cm^{-1})		^1H NMR[b]	^{121}Sb NMR[c]		Electronic[d] λ_{max} (cm^{-1})
	C	H	Cl				δ (ppm)	$W_{1/2}$ (Hz)	
$[(H_3O)(18\text{-crown-6})][SbCl_6]$ (**I**)	23.4	4.4	34.4	1287	1250	3.67	−0.10	253.39	37,023
	(23.3)	(4.4)	(34.4)	1141	1094	10.10			
				1077	970				
				946	839				
				723	338				
				266					
$[(H_3O)(12\text{-crown-4})_2][SbCl_6]$ (**II**)	27.3	4.9	30.1	1298	1287	3.63	−0.12	248.62	37,091
	(27.2)	(5.0)	(30.1)	1242	1132				
				1090	1020				
				914	845				
				716	550				
				338	260				
$SbCl_3{\cdot}15\text{-crown-5}$ (**III**)	26.8	4.6	23.6	1314	1304	3.77			
	(26.8)	(4.5)	(23.7)	1241	1134				
				1110	1094				
				1078	1064				
				1046	1039				
				1024	932				
				850	818				
				808	788				
				722	580				
				560	542				
				506	322				
				280					
$[(H_3O)(15\text{-crown-5})][SbCl_6]$ (**IV**)				1305	1291	3.61	−0.13	244.53	37,050
				1252	1135				
				1095	1073				
				1022	958				
				919	340				

[a] ν (cm^{-1}) for nujol mull. [b] δ (ppm) for CD_3CN solutions with tetramethylsilane as internal reference. [c] δ (ppm) for CH_3CN solutions (*c.* 10^{-2} M) doped with 10% (by volume) of CD_3CN with $[Et_4N][SbCl_6]$ ($\delta = O$, $W_{1/2}$, 190 Hz) as external reference. A negative δ value indicates an upfield chemical shift with respect to $SbCl_6^-$. [d] CH_3CN solutions *c.* 1×10^{-3} M concentration.

the cation is proposed but, clearly, the same type of symmetrical hydrogen bonding as observed in the $[(H_3O)(18\text{-crown-6})]$ counterpart is no longer feasible. For comparison $NaOH{\cdot}(12\text{-crown-4})_2{\cdot}8H_2O$ [21] and $NaCl{\cdot}(12\text{-crown-4})_2{\cdot}5H_2O$ [22] each contain a $[(Na)(12\text{-crown-4})_2]^+$ cation unit in which the metal ion is sandwiched between two cyclic rings.

(c) Reaction with 15-crown-5

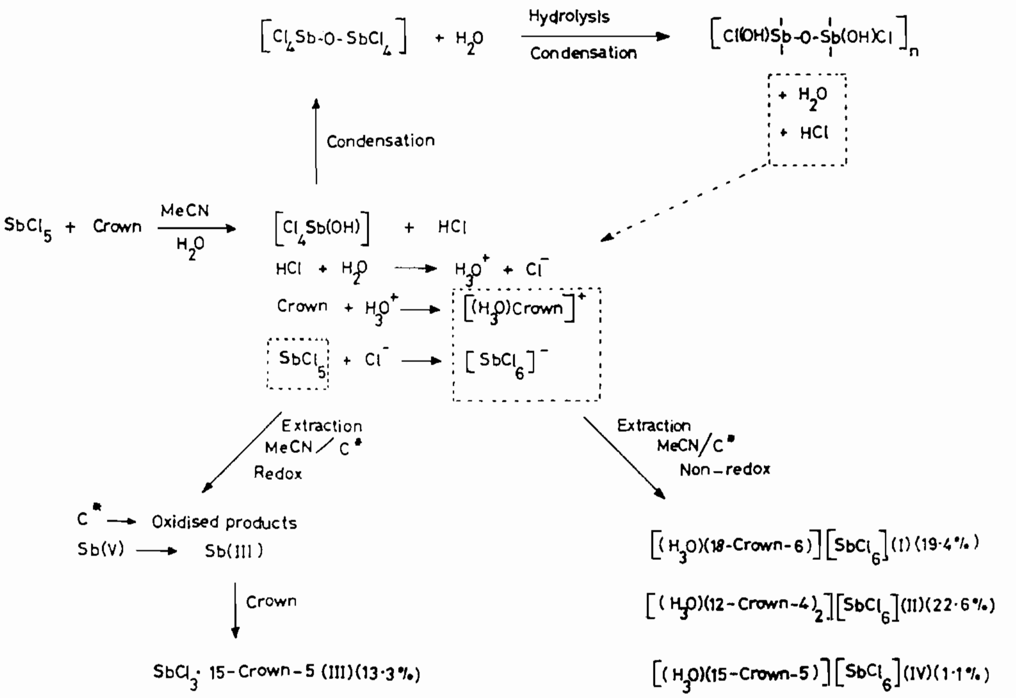
The light yellow solution resulting from the final extraction with MeCN/activated charcoal yielded colourless crystals of the 1:1 tervalent adduct $SbCl_3{\cdot}15\text{-crown-5}$ (**III**) [2] and a minute crop (*c.* 1%) of pale yellow crystals of the (assumed) hydronium ion–crown ether (1:1) complex $[(H_3O)(15\text{-crown-5})])[SbCl_6]$ (**IV**). Spectroscopic and analytical data are listed in Table 1.

The ^1H NMR spectrum of **III** consists of one sharp signal for ring protons δCH_2 3.77 (uncomplexed ligand δ3.57). In the IR spectrum the two strong ligand bands ν(C–O–C) at 1112 and 1090 cm^{-1} assume a sharp multiplet pattern 1134, 1110, 1094 and 1078 (doublet) and 1064 cm^{-1} and bands at 322, 280 cm^{-1} are assigned to ν(Sb–Cl) vibrations.

For **IV** spectroscopic evidence in the form of intense ν(Sb–Cl) 340 cm^{-1} (IR) and charge-transfer λ_{max} 37 050 cm^{-1} (Vis–UV) bands and a clearly resolved singlet δ −0.13 ppm (^{121}Sb NMR) confirm the formation of an antimonate salt which, in the absence of satisfactory microanalyses, we assume to be of 1:1 stoichiometry, viz. $[(H_3O)(15\text{-crown-5})][SbCl_6]$. The ^1H NMR spectrum shows ring protons δCH_2 3.61 ppm but we were unable to locate the cation $(H_3O)^+$ protons. Heo and Bartsch [13] have reported the formation of an ill-defined and difficult-to-handle $[H_3O^+\text{-}15\text{-crown-5}]$ complex, which answers neither to 1:1 nor 1:2 stoichiometry, following addition of concentrated aqueous HPF_6 to a CH_2Cl_2 solution of 15-crown-5.

General comments

The main point of interest arises from the separate reaction routes observed: formation of



Scheme 1.

antimon(v)ate salts and, in the case of L = 15-crown-5, accompanying redox formation of the neutral Sb(III) complex $SbCl_3 \cdot L$ (Scheme 1). The yields in each case are less than 25% (based on the $SbCl_5$ used). For the former, limited hydrolysis of $SbCl_5$ initiated by an adventitious presence of H_2O, most probably from the crown ether used, can be viewed as the dominant reaction. Inclusion of water molecules by crown ethers has been noted [23] particularly for 18-crown-6 where a well-defined hydration complex 18-crown-6:(4–6)H_2O has recently been described [24]. Onset of Sb–Cl hydrolysis involving either solvated $SbCl_5 \cdot MeCN$ or weakly-complexed $SbCl_5 \cdot (crown)_x$ species—and hence the initial yellow solution formation—leads to formal [$SbCl_4(OH)$] species and the release of HCl as the primary source of both cation [$H^+ + H_2O$] and anion [$SbCl_5 + Cl^-$]. Condensation of formal [$Sb(OH)Cl_4$) species releases yet more H_2O and formation of μ-oxo-chloro[Sb–O–Sb] oligomeric/polymeric species which, of themselves, are susceptible to Sb–Cl hydrolysis reactions with release of further H_2O and HCl etc. With a negligent amount of water present and hence absence of Sb–Cl hydrolysis to any recognisable extent, redox formation of Sb(III) involving $SbCl_5$(oxidant) ~ activated charcoal (reductant) now becomes the dominant reaction. The powerful oxidising capacity of Sb(V) is well recognised [25]. Again the observation that **I** and **II** can be recrystallised unchanged from acetonitrile/activated charcoal solutions would seem to preclude any redox action involving $SbCl_6^-$ either directly or indirectly via regeneration of free $SbCl_5$ and chloride ion.

The two pathways are clearly not mutually exclusive and, as observed in the case of $SbCl_5$/15-crown-5, both can be involved to a lesser or greater degree. In our view the critical factor in these systems which determines the final outcome, i.e. antimon(v)ate salt versus Sb(III) complex formation is the extent of water present both initially and as sustained *in situ* via condensation/hydrolysis reactions. In the case of 18-crown-6/$SbCl_5$, addition of water (0.1 cm^3) at the outset to assist controlled solvolysis reactions resulted in an increased yield of **I** (27.7%).

An insight of the relative complexing abilities of 12-crown-4, 15-crown-5 and 18-crown-6 with the hydronium ion is provided by the thermochemical datal, ΔH (enthalpy) and ΔS (entropy), obtained by Sharma and Kebarle [26] from measurements of the ion–molecule equilibria crown $+ H_3O^+ \longrightarrow$ [crown(H_3O)]$^+$ in the gas phase. Whereas the formation of an [18-crown-6(H_3O)]$^+$ complex accommodating three strong hydrogen bonds $O\text{–}H^+_{cation} \cdots O_{ring}$ with three alternate ring oxygen atoms is the most favoured ($-\Delta H$ 88.5 kcal/mol, $-\Delta S$ 55.8 eu), formation of an [15-crown-5(H_3O)]$^+$ complex ($-\Delta H$ 76.9 kcal/mol, $-\Delta S$ 43.2 eu) though less favourable is clearly not excluded. For the latter two bonding arrangements have been mooted: either two strong O–H$^+_{cation}\cdots O_{ring}$ hydrogen bonds aided by favourable –CH$_2$–O–CH$_2$– dipole orientations together with a third severely weakened hydrogen bond to a third oxygen atom of the ring or three nearly equivalent but somewhat weakened O–H$^+_{cation}\cdots O_{ring}$ hydrogen bonds implicit with a distorted structure. In either case only three of the five available ring oxygen atoms are directly involved in hydrogen bonding. Significantly for [12-crown-4(H$_3$O)]$^+$ complex formation, exact values for enthalpy/entropy changes could not be obtained due to interference by the further equilibrium 12-crown-4 + [12-crown-4(H$_3$O)]$^+$ $\longrightarrow$ [(12-crown-4)$_2$H$_3$O]$^+$. The successful isolation of **II** and [(H$_3$O)(12-crown-4)$_2$[PF$_6$] [13] as stable complexes comes as no great surprise. An X-ray crystal structure determination of **II** is now in progress [27].

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