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The trimethylantimony cation

Examination of the crystal structures[1] and infrared spectra[2] of solid trimethylantimony(V) derivatives of the type $(CH_3)_3SbX_2$ has tended to underline the molecular nature of these systems, although the trigonal bipyramidal array of ligands associated with each antimony atom does not necessarily imply that the compounds are molecular since covalent or electrostatic interactions would probably favour similar models. No evidence has yet been advanced for the existence of the discrete trimethylantimony cation, $(CH_3)_3Sb^{2+}$; the isoelectronic trimethyltin(IV) cation, $(CH_3)_3Sn^+$, while it gives rise to polymeric 5-co-ordinate networks in the solid phase[3], apparently forms a simple aquated species in aqueous solutions[4,5]. Since the behaviour of trimethylantimony(V) salts under aqueous conditions has been little explored, we have examined the Raman spectra of aqueous solutions of trimethylantimony dinitrate and diperchlorate to elucidate the nature of the solute species.

Trimethylantimony dinitrate and diperchlorate, prepared by methods described elsewhere[2], gave clear 1.0–2.0 *M* aqueous solutions. Raman spectra of high quality were obtained using a Cary Model 81 spectrometer with Hg 4358 Å excitation; the addition of small amounts of the parent acids seemed not to affect the results which are presented in Table 1. Two important conclusions are immediately evident:

TABLE 1

RAMAN SPECTRA OF AQUEOUS SOLUTIONS OF TRIMETHYLANTIMONY DINITRATE AND DIPERCHLORATE

$Me_3Sb(ClO_4)_2$		*$Me_3Sb(NO_3)_2$*		*Origin*	*Symmetry species*	*Approximate description of mode*
cm^{-1}	*Intensity, pol.*[a]	*cm^{-1}*	*Intensity, pol.*			
3034	s,br,dp	3034	s,br,dp	Me_3Sb	e' or e''	C–H antisym. stretch
2939	vs,p	2940	vs,p	Me_3Sb	a'_1	C–H sym. stretch
1408	vw,br	1409	w,br	Me_3Sb	e' or e''	CH_3 antisym. deform.
		1386	w,sh	NO_3^-	e'	NO_2 stretching
1249	ms,p	1249	m,p	Me_3Sb	a'_1	CH_3 sym. deform.
1236	m,sh,dp	1237	m,sh,dp	Me_3Sb	e'	CH_3 sym. deform.
1098	w,br			ClO_3^-	f_2	ClO stretching
		1048	s,p	NO_3^-	a'_1	NO stretching
932	vs,p			ClO_4^-	a_1	ClO stretching
830	vw			Me_3Sb	e'	CH_3 rocking
		716	w,br	NO_3^-	e'	NO_2 bending
		675	vvw	Me_3Sb	e''	CH_3 rocking
623	mw,dp			ClO_4^-	f_2	ClO_2 antisym. bend
585	s,dp	582	s,dp	Me_3Sb	e'	Sb–C antisym. stretch
537	vs,p	536	vs,p	Me_3Sb	a'_1	Sb–C sym. stretch
461	m,dp			ClO_4^-	e	ClO_2 sym. bend
168	s,dp	166	s,dp	Me_3Sb	e'	SbC_3 in-plane deform.

[a] s = strong, w = weak, m = medium, v = very, br = broad, sh = shoulder, p = polarised, dp = depolarised.

(i) The vibrational bands characteristic of the oxyanions are essentially the same as those reported for aqueous solutions of simple ionic nitrates and perchlorates[6,7], and in particular we note the absence of splitting or broadening of bands due to doubly or triply degenerate modes. Since co-ordination of perchlorate or nitrate ions leads usually to significant changes in the vibrational spectra[6,8] it is a fair inference that there is no *strong* interaction involving the anions beyond the possible formation of ion-pairs (which would be expected to lead to only minor modifications of the Raman spectra of the anions and no additional scattering of measurable intensity)[9].

(ii) Once the lines characteristic of the anions have been eliminated in each case, the spectra indicate a methyl–antimony cationic species common to the two solutions. As the methyl–antimony bonds are not measurably hydrolysed under these conditions the basic unit is presumably $(CH_3)_3Sb^{2+}$ although this may exist either in the form of a simple aquated cation (I) or of a partially hydrolysed entity such as $[(CH_3)_3SbOH]^+$ (II) or $[(CH_3)_3Sb{\cdot}O{\cdot}Sb(CH_3)_3]^{2+}$ (III).

The general simplicity of the spectrum of the cation with just three polarised lines supports the presence of a planar $(CH_3)_3Sb$ unit. This is consistent with I, for species II and III would require appreciably more complicated spectra, apart from which they presumably involve a pyramidal SbC_3 unit. In principle a planar SbC_3 skeleton (D_{3h} symmetry) should give three Raman lines due to fundamental vibrations (one being polarised); in the region below 700 cm^{-1} the observed spectra comply exactly with these rules. By contrast, a pyramidal SbC_3 skeleton (C_{3v} symmetry) possesses four Raman-active fundamentals (two of which should give polarised Raman lines). In practice this distinction between the two systems is rarely as clearcut as it seems. The essential difference in the Raman spectra hinges on the deformation modes of the skeleton; for the planar unit only one depolarised line is expected, whereas for the pyramidal unit there should be two lines one of which is polarised. In pyramidal molecules of the type $M(CH_3)_3$ (M = N, P, As, Sb or Bi) the two deformation frequencies become more nearly degenerate as the mass of the central atom increases so that for $(CH_3)_3Sb$ it is impossible to resolve the two low-frequency deformation lines[10]. Simultaneously the frequencies of the symmetric (ν_s) and antisymmetric (ν_a) M–C stretching vibrations also become virtually degenerate for the heavier central atoms like antimony and bismuth since both vibrations involve appreciable motion of the atom M. ν_s and ν_a of analogous planar molecules are invariably well separated in frequency (*cf.* $Ga(CH_3)_3$ and $In(CH_3)_3$[11]); this is understandable as long as vibrational coupling is absent since ν_s involves little or no movement of the central atom. Therefore whereas the number of bands in the deformation region may be an ambiguous criterion of symmetry, the frequency separation of the two skeletal stretching modes can be informative. Comparison of $\nu_s = 537$ cm^{-1} and $\nu_a = 584$ cm^{-1} for the trimethylantimony cation with (a) $\nu_s = \nu_a = 514$ cm^{-1} for $(CH_3)_3Sb$[10] and (b) $\nu_s = 522$ cm^{-1} and $\nu_a = 570$ cm^{-1} for $(CH_3)_3Ga$[11] gives grounds for believing that the SbC_3 framework of the cation is essentially planar.

Assignments of the observed Raman frequencies of the $(CH_3)_3Sb^{2+}{\cdot}aq.$ cation are possible on the strength of the D_{3h} selection rules, and by analogy with molecules like $(CH_3)_3Ga$ and $(CH_3)_3In$[11]. The force constants, *k*, of the M–C bonds in the isoelectronic series $(CH_3)_3In$, $(CH_3)_3Sn^+$ and $(CH_3)_3Sb^{2+}$, evaluated on the assumption of a simple valence force field (each CH_3 group being regarded as a single "atom" of mass 15 atomic units), increase with positive charge; though the increments in *k* are relatively disparate, the sequence follows the general behaviour of other isoelectronic series and stands in marked contrast to the only other comparable triad of heavy metal methyl derivatives for which data are available, *viz.* $(CH_3)_2Hg$, $(CH_3)_2Tl^+$ and $(CH_3)_2Pb^{2+}$ (see Table 2)[5]. Presumably variations in k reflect solvation effects as well as intrinsic properties of the M–C bond, but without more information the relative importance of the two terms cannot be assessed.

TABLE 2

FORCE CONSTANTS FOR M–C BONDS OF ISOELECTRONIC SEQUENCES OF HEAVY METAL DI- AND TRI-METHYL SYSTEMS.

System	*Sym. M–C stretching frequency* (cm^{-1})	k_{M-C} $\times 10^5$ *dynes/cm*	*Reference*
$(CH_3)_2Hg$	514	2.46	5
$(CH_3)_2Tl^+$	498	2.29	5
$(CH_3)_2Pb^{2+}$	479	2.11	5
$(CH_3)_3In$	467	1.93	5
$(CH_3)_3Sn^+$	520	2.39	5
$(CH_3)_3Sb^{2+}$	537	2.55	present work

Reference to the infrared and Raman spectra of solid anhydrous trimethylantimony dinitrate reveals a very different situation from that of the aqueous solution. Our results confirm earlier conclusions based on infrared data[2] that the nitrate ions are now strongly co-ordinated to the metal atom. The dramatic changes in the spectra of the anion compared with that of a "free" nitrate ion are similar to those observed for molecular nitrates[6], and this molecular character is emphasised by the fact that the anhydrous dinitrate is comparatively volatile (subliming without decomposition *in vacuo* at 120° C). Present evidence indicates that the basic unit in the solid state and in non-polar solvents is a trigonal bipyramidal monomer with the nitrato groups in axial positions.

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