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Vibrational Spectroscopy of Bromoantimonate(III) Complexes

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Vibrational spectra are reported for a number of bromoantimonate(III) complexes. The spectra obtained showed a surprisingly large variation even between compounds with the same stoichiometry. Assignments have been made in terms of antimony–bromine terminal and bridging stretching modes in addition deformation and lattice vibrations. An interpretation of the results rests heavily on the limited structural information available, but in the main the experimental data is indicative of a highly distorted octahedral environment in these compounds.

Introduction

This paper describes vibrational spectra obtained for a number of single valence halo-coordinated antimony(III) compounds. In view of the variability in stoichiometry encountered for known black bromoantimonate complexes prepared with aliphatic and aromatic amines as counter ions [1], particular attention has been focussed on the compounds formed between antimony(III) bromide and various hydrobromides.

Experimental

Preparation of Bromoantimonate(III) Complexes

The compounds R_2SbBr_5 (R = piperidinium, β-picolinium, γ-picolinium, pyridinium, ethylammonium or n-butylammonium), $RSbBr_4$ (R = α-picolinium or pyridinium), R_3SbBr_6 (R = di-ethylammonium or di-n-propylammonium) and $R_3Sb_2Br_9$ (R = tetraethylammonium) were prepared by slight variations of the method described by Whealey and Yeakley [1]. Antimony(III) bromide solution was prepared by dissolving reagent grade antimony trioxide in an excess of hot hydrobromic acid (15g, Sb_2O_3 in 70 ml, HBr (47%)). The amine hydrobromides were prepared by adding a two-fold excess of hydrobromic acid to the amine. In certain cases precipitation of the bromide occurred, and sufficient 95% ethanol was then added to dissolve any salt. Aliquot portions of the solutions were used such that approximately ten mol of amine hydrobromide was added to each mole of antimony(III) bromide. The complex salts usually formed immediately, but for a number of cases it was necessary to immerse in a salt/ice bath before crystallization commenced. The resulting crystals were separated by vacuum filtration through a Buckner funnel and rinsed with isopropanol and then with diethyl ether. The compounds were crystallized from acetone, and on occasions ethanol. The products were washed with ether and dried in a vacuum desiccator.

Whealy and Yeakley report that for a particular amine the nature of the complex salt produced is constant, and only the yield is affected by the antimony/amine molar ratio. This does not appear to be always so, and for a number of amines the salt obtained is governed rather finely by the exact conditions used. Thus the α-picolinium complex is initially precipitated in a bright yellow form but is converted to a paler form on standing. Two distinct pyridinium complexes have been isolated; R_2SbBr_5 (yellow) $RSbBr_4$ (pale yellow). A mixture of the two forms is usually precipitated from aqueous solution, but by varying the conditions it is possible to produce predominently the paler form. The yellow form can be purified by crystallization from acetone, whereas ethanol was found to yield the paler form. A third form ($R_5Sb_2Br_{11}$) has been reported and its structure solved by Porter and Jacobson [2]. However, attempts to repeat their preparation were unsuccessful. All of the compounds gave satisfactory analyses for C, H, N and Br and where possible melting points were checked against the literature values [1].

Infrared Measurements

Infrared spectra were recorded using a Perkin Elmer 225 spectrophotometer and a Grubb-Parsons IRIS interferometer. The Perkin Elmer 225 allowed spectra to be recorded in the range 4000–200 cm^{-1}. The range of interferometer depended on the source window, and the beam splitter used. It was adjusted to cover the range ~50–300 cm^{-1}. Samples for the

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TABLE I. Infrared Data.

Compound		Terminal Stretches					Bridging Stretches			Deformation and Lattice Modes
R_2SbBr_5	R		211(s),	204(sh?),	189(m)			137(w)		60(m)
R = piperidinium	I.R	249(m)[a],	210(sh),	203(m),		169(s.b)		~130(s.pl)		73(sh), 56(sh), 33(m), 24(s)
R_2SbBr_5	R		206(s),		192(s)	167(w)		133(w)		75(w), 61(w), 48(w), 40(w), 31(s)
R = β-picolinium	I.R	230(m)[a],		197(sh),	187(s)	160(s.b)	130(sh)		101(m)	53(m.b)
R_2SbBr_5	R		207(s),		192(m)			130(w)		85(sh), 60(sh)
R = pyridinium										
R_2SbBr_5	R		206(s),		190(m.s)			144(w)		95(sh), 59(sh), 39(s)
R = n-butylammonium										
R_2SbBr_5	R		205(s)		187(m)		137(w)		93(w)	61(m), 39(s)
R = ethylammonium	I.R		200(sh?)		175(s.b)			100(s.b)		~60(m)
R_2SbBr_5	R		190(s)		170(s)	152(sh)	136(w),	115(w.sh)	107(m.sh)	78(sh), 69(sh), 62(m), 45(s) 32(s), 26(s)
R = γ-picolinium	I.R	228(m)[a],		183(sh)	174(s)	152(sh)	137(sh),	127(sh),	94(m)	75(w), 71(w), 66(w)
$RSbBr_4$	R	224(s),	218(s),	204(s),	196(m)		142(m.b),	125(sh.b)		97.5(m), 80.5(s), 65(sh), 60(ms), 57(m), 46(m), 37(s), 28(s)
R = α-picolinium	I.R	224(sh),		203(s),	191(m)		149(m.b),	126(m.b)		107(sh), 102(sh), 95(s)
$RSbBr_4$	R	218(s),	210(m)					128(w)		97(sh), 87(m), 62(s), 50(s), 33(sh), 28(m)
R = pyridinium	I.R	220(sh?)	211(s)					146(m.b)		97(m)
R_3SbBr_6	R	220(sh)[b],	149.5(s)		129(s)					96(m)
R = di-n-propylammonium	I.R			145(s.b)						60(m)
R_3SbBr_6	R			178(s.b)						104(w.sh), 70(m), 54(s), 44(m)
R = di-ethylammonium	I.R			178(s.b)						72(w), 54(w)
$R_3Sb_2Br_9$	R			201(s.b)				155(s.b)		115(m.b)
R = tetraethylammonium	I.R			199(s),	184(sh)			152(sh)		112(m)
$R_3Sb_2Br_9$	R			201(sb),	185(s.b)					60(sh), 49(sh), 32(s)
R = methylammonium	I.R.				176(s.b)			115(s.b)		61(m)

[a] Peak assigned to cation (present in other salts). [b] Probably due to impurities. Abbreviations used are: s, strong; m, medium, w, weak; b, broad; sh, shoulder; pl, plateau.

Perkin Elmer were prepared as nujol mulls and smeared between CsI plates with thin polythene sheets as protective liners. Samples for the IRIS were prepared as vaseline mulls, which were sandwiched between polythene discs in a special holder.

Raman Measurements

Raman spectra were recorded using a Coderg PHO spectrometer with a Krypton laser. Yellow light (568.2nm) was used as source radiation for the present samples which were mounted as powders either in melting point tubes or a cone sample holder.

Results and Discussion

The spectra obtained showed a surprisingly large variation even between compounds with the same stoichiometry. The results are summarised in Table I. An interpretation of these results reacts heavily on the limited structural information available. X-ray data is available for a number of analogous bismuth complexes [3–5] and results have also been reported for the compound bispiperidinium pentabromoantimonate(III) [6].

R_2SbBr_5 Compounds

Bispiperidinium pentabromoantinonate(III) has a bridged polymeric structure which is very similar to that of the isomorphons bismuth complex [3]. The form of the Sb chains is shown schematically in Figure 1. The figure also gives details of Sb–Br and Bi–Br bond lengths in the respective structures. The angles between the *cis*-bromine atoms are all close to 90°; ranging from 87.3° to 93.4° for the Sb complex.

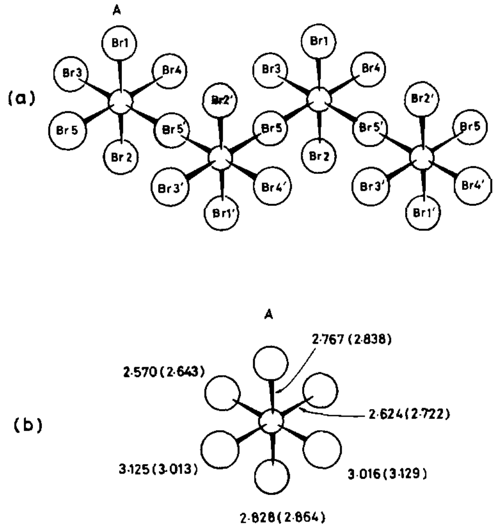

Figure 1. (a) Structure of bispiperidinium pentabromoantimonate(III), showing the metal–halogen chains. (b) Bond distances for unit A (those for the corresponding bismuth salt in brackets).

An idealized limit of this structure would be one in which all bridging, all equatorial (to Br1 and Br2) and all axial (to Br3 and Br4) bond lengths were the same. Although this condition is not fulfilled in these complexes the expected ordering of bond lengths (bridging > axial > equatorial) is observed. In the idealized structure the symmetry round the metal would be C_{2v} with two possible A_1 (axial and equatorial), one B_1 (equatorial) and one B_2 (axial) bromine stretching modes. There should be some mixing between the A_1 modes, but even so it would be reasonable to think in terms of symmetry and assymmetry of axial and equatorial modes. Such an analysis, however, is probably inappropriate for the unsymmetrical structure of bispiperidinium pentabromoantimonate(III). For this reason assignments are given in Table I with respect to terminal and bridging stretching modes only. The spectra of the other R_2SbBr_5 complexes (R = pyridinium, n-butylammonium or ethylammonium) are very similar and assignments for individual bands can be carried over from the piperidinium complex. Table I also shows that it is possible to relate the bands of the Raman and infrared spectra of the β-picolinium complex. If the Raman spectra are compared the intensity ratios of the high energy bands are found to differ, but the positions of the high energy band envelopes are very similar.

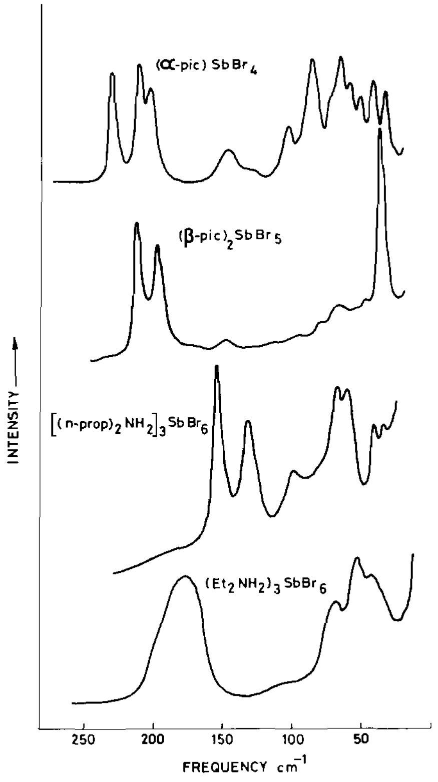

Figure 2. Raman spectra of some bromoantimonate(III) complexes.

As Figure 2 shows, the best resolved Raman spectrum was obtained from bis-β-picolinium pentabromoantimonate(III) especially in the region of the very sharp feature at 31 cm^{-1}. It is possible that this is associated with greater symmetry at the Sb centres. Although the Raman and infrared spectra of the γ-picolinium complex show a certain resemblance to those of the β-picolinium complex, (see Figures 2 and 3), there is however, a distinct shift to lower energy in the terminal stretch part of the spectrum, and greater complexity at low energy. It is tempting to assume a high symmetry structure for the β-picolinium compound, which is subject to various types of distortion in other R_2SbBr_5 complexes, but further X-ray data is required to eliminate the possibility of radically differing structure types and a comprehensive assignment of individual bands is precluded by the limited structural information presently available.

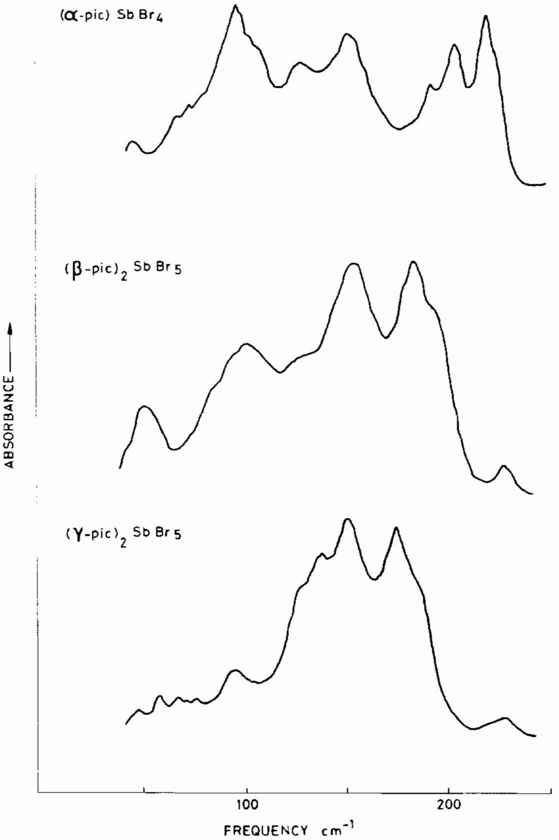

Figure 3. Infrared spectra of α-picolinium, β-picolinium and γ-picolinium bromoantimonate(III) complexes.

$RSbBr_4$ Compounds

Two compounds with the stochiometry $RSbBr_4$ were prepared (R = α-picolinium or pyridinium). The crystal structure is available for the bismuth analogue of the α-picolinium complex [5]. There is a strong possibility that the Bi and Sb compounds are isomorphous, especially considering the piperidinium complexes mentioned in the previous paragraph. α-picolinium tetrabismuthate(III) has the polymeric structure shown schematically in Figure 4. Here again all of the angles between *cis*-bromines are close to 90°. The bond lengths for this compound are included in Figure 4 together with those for pyridinium tetrachloroantimonate(III), which has a closely related structure [7]. The structural data for the pyridinium complex can be viewed in two ways. Thus Porter and Jacobson [7] considered that the Sb atom was at the centre of a distorted octahedral arrangement of chlorine atoms in $[C_5H_5NH][SbCl_4]$ whereas in the same compound Ahlijah and Goldstein [8] visualized the presence of a distinct $SbCl_4^-$ grouping with the idealized trigonal bipyramidal structure (here the presence of a stereochemically active lone pair in the equatorial position was assumed).

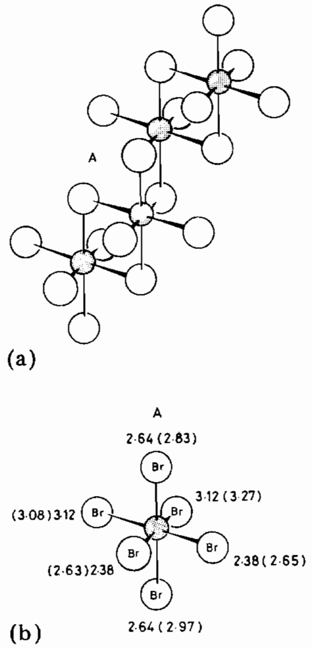

Figure 4. (a) Structure of α-Picolinium tetrabromoantimonate(III), showing the metal–halogen chains. (b) Bond distances for unit A (those for pyridium tetrachlorobismuthate(III) in brackets).

As Figures 2 and 3 show the infrared and Raman spectra of α-picolinium tetrabromoantimonate(III) exhibit four sharp bands, which can reasonably be assigned to terminal stretches. The rather less well resolved features at ~145 and ~125 cm^{-1}, are probably associated with bridging stretches. If the presence of fairly regular trigonal bipyramidal $SbBr_4^-$ groups in the structure is assumed the most reasonable assignment would associate the bands at 218 and 196 cm^{-1} with the assymmetrical and symmetrical axial stretches. The equatorial stretches could then be ascribed to the bands at 224 and 204 cm^{-1}. Such an assignment is based on the following observations [9]. (i) Symmetrical axial stretches tend to be strongly Raman active, but weakly infrared active. (ii) The separation between the axial modes is usually greater than that between the equatorial modes.

A knowledge of the spectrum of the isolated $SbBr_4^-$ species would give some indication as to the correctness of this assignment. Ahlijah and Goldstein have recorded Raman spectra from $N(n\text{-}but)_4SbBr_4$ in the solid state and in solution in CH_2Cl_2 and CH_3NO_2. A reinvestigation of this system [10] shows, however, that their results are open to question.

The spectrum of pyridinium tetrabromoantimonate shows only two resolvable bands in the terminal stretch region. This may be a consequence of the near coincidence of the four bands, but it seems more likely, though that this compound has a completely different structure. Other forms of polymeric chain structures are likely, but the presence of a dimeric species $[Sb_2Br_8]^{2-}$ remains a possibility. Groupings of this kind have been identified in the structure determination of $Bi_{12}Cl_{14}$ [11], and consist of pairs of tetragonal pyramids sharing a base edge.

R_3SbBr_6 Complexes

Two complexes with the empirical formula R_3SbBr_6 have been studied, the diethylammonium and the di-n-propyl-ammonium compounds. A structural determination is available for $(Et_2NH_2)_3$-$BiBr_6$, which contains two crystallographically distinct $BiBr_6^{3-}$ sites, both closely octahedral [4]. The corresponding Sb compound is thought to be isostructural on the basis of X-ray powder evidence [12]. The spectra obtained for the di-n-propylammonium compound are rather different from those for the di-ethylammonium compound, (see Figure 5). They are, however, similar to those obtained for $Co(NH_3)_6SbBr_6$, which has been interpreted in terms of a regular octahedron [13]. Thus the two Raman active bands at 149.5 and 129 cm^{-1} are assigned to $\nu_1(a_{1g})$ and $\nu_2(e_g)$ modes and the infrared active band at 145 cm^{-1} to the $\nu_3(t_{1u})$ mode. The corresponding bands in the $Co(NH_3)_6SbBr_6$ spectra are at 159, 137 and 141 cm^{-1}. These spectra are a little unusual for octahedral species in a number of respects. (i) The usual ordering of transitions ($\nu_3 > \nu_1 > \nu_2$) is not observed. This may be because only ungerade vibrational modes will remove the centre of inversion of the system, lowering the energy of the antibonding a_{1g} orbital through mixing with low lying p-orbitals. This effect will tend to reduce the energy required to deform by the ν_3 but not by the ν_1 and ν_2 modes.* (ii) The intensity ratio (ν_2/ν_1) is rather high compared to say $SnBr_6^{2-}$, which displays what might be considered normal octahedral behaviour [13]. (iii) The ν_3 mode is unusually broad. This might be due to loss of degeneracy of this band together with certain infrared activity of the ν_1 and ν_2 modes. It probably indicates a slight reduction in symmetry below O_h. Such an effect might also account for the unusual (ν_2/ν_1) intensity ratio.

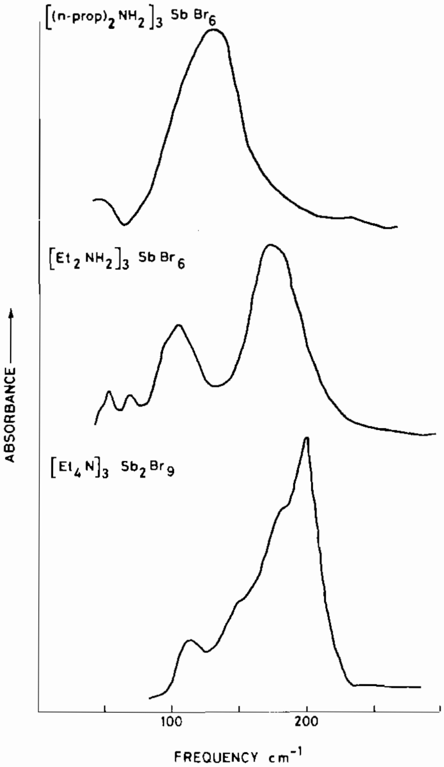

Figure 5. Infrared spectra of some aliphatic bromoantimonate(III) complexes.

The infrared and Raman spectra of $(Et_2NH_2)_3$-$SbBr_6$ are very broad and unresolved. They are also very similar in form, indicating considerable overlap of bands which are probably active in both the infrared and Raman. Some distortion removing the centre of inversion is indicated. Judging by the Raman spectrum in aqueous HBr [13] a similar configuration for the $SbBr_6^{3-}$ species is probably found in this medium. An important feature in the spectra of these distorted species, as opposed to the more regular form proposed for $(n\text{-}propNH_2)_3SbBr_6$ is the general shift to higher energy for the bromine

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*If this process occurred it would be interesting to speculate as to whether such a mechanism would be applicable to non-centrosymmetric systems. If so, the arguments used in relation to symmetric and assymmetric modes in R_2SbBr_5 and $RSbBr_4$ systems have to be modified.

stretching frequencies; an effect which may be associated with mixing in of p-character reducing and anti-bonding nature of the A_{1g} orbital.

$R_3Sb_2Br_9$ Complexes

Also included in Table I are spectral details for compounds $R_3Sb_2Br_9$ (R = Et_4N^+ and $MeNH_3^+$). The spectra of these two compounds are rather similar in general appearance (the infrared spectral of the tetraethylammonium complex is reproduced in Figure 5). There are, though appreciable shifts in the position of the bands. Discrete $Sb_2Br_9^{3-}$ units appear in the structure of $R_5Sb_2Br_{11}$ (R = pyridinium) [2]. However, as mentioned above, attempts to make this compound were unsuccessful. In the methylammonium complex there is the distinct possibility of a three dimensional network of bridging bromines, without distinctly discrete $Sb_2Br_9^{3-}$ units. Such arrangements have been found for $Cs_3As_2Cl_9$ [14] and $Cs_3Sb_2Cl_9$ [15]. With the larger cation in the tetraethylammonium complex there is a greater probability for discrete units.

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