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Raman Studies of the $SbBr_3/(n\text{-}but)_4$ NBr System in Dichloromethane

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Recently ther has been considerable interest in the vibrational spectra of both single valence and mixed-valence halo-coordinated antimony compounds [1–4]. Definitive assignments for the spectra of compounds of type $RSbBr_4$ would be greatly aided by a knowledge of the Raman and infrared spectra of the isolated $SbBr_4^-$ species. Ahlijah and Goldstein have published Raman data for $(n\text{-but})_4SbBr_4$ dissolved in both CH_2Cl_2 and $MeNO_2$ [1]. We report here a similar study in which various $SbBr_3/Br^-$ concentration ratios have been used with a view to establishing whether the spectra are representative of a discrete species or some kind of mixture.

Experimental

Raman spectra were recorded using a Coderg PHO spectrometer with a Krypton laser. Yellow light (568.2nm) was used as source radiation. Reagent grade $SbBr_3$ (Hopkin and Williams) and $(n\text{-but})_4NBr$ (Eastman-Kodak) were used in various molar ratios dissolved in dichloromethane which had been freshly distilled from P_2O_5. Runs were made using two different $SbBr_3$ molar concentrations (0.12*M* and 0.1*M*), but there appeared to be little concentration dependence in the form of the spectra.

Results and Discussion

Raman spectra recorded from solutions containing $SbBr_3$ and Br^- in a number of molar ratios are shown in Figure 1. Here spectra of solutions with the same Sb molar concentration have been taken using identical instrumental settings.

Figure 1(a) shows the spectrum of $SbBr_3$. From a consideration of intensity and polarisation data, and assuming C_{3v} symmetry for the species in solution, the band at 248cm^{-1} can be assigned to the A_1 and the shoulder at ~249cm^{-1} to the E stretching mode. When bromide is added to this solution the species formed initially is probably $Sb_2Br_7^-$.

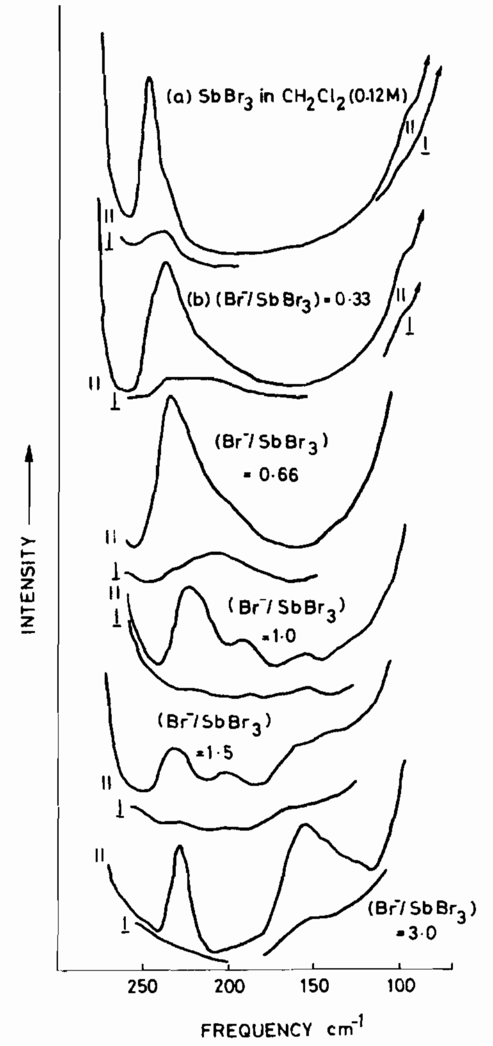

Fig. 1. Raman spectra of some solutions of antimony(III) bromide in dichloromethane.

As can be seen from Figures 1(b) and 1(c) the parent $SbBr_3$ peak is still discernible for a $(Br^-/SbBr_3)$ molar ratio of 0.33, but is no longer apparent when this ratio is increased to 0.66. The spectrum obtained for a molar ratio of 1.0 (Figure 1(d)) is in good agreement with that published by Ahlijah and Goldstein [1]. However, it still contains the feature at ~235 cm^{-1} which can be attributed to $Sb_2Br_7^-$. The bands at 203 and 165cm^{-1} may be due to the $SbBr_4^-$ species (with the possibility of a partially obscured band at higher energy). The presence of other species cannot be discounted readily though, especially when the spectrum attributed to the $Sb_2Br_9^{3-}$ species in $(Et_4N)_3Sb_2Br_9$ is considered [5]. This compound shows strong broad maxima in the Raman spectrum at a frequency of 201 and 155cm^{-1} with a weaker

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band at 115cm^{-1}. The addition of further bromide leads to a reduction and change in shape of the band at ~158cm^{-1}. The limiting spectrum (Figure 1(f)) formed with a molar ratio of ~3.0 is the same as that published by Adams and Downs [5], and very likely corresponds to the species $SbBr_6^{3-}$. Certainly if $Sb_2Br_9^{3-}$ is formed it is not exclusively present in a solution with a ($Br^-/SbBr_3$) molar ratio of 1.5, where it would appear there is an equilibrium concentration of $SbBr_6^{3-}$. Two limiting representations for the reaction scheme would be:

$$2SbBr_3 \overset{Br^-}{\rightleftharpoons} Sb_2Br_7^- \overset{2Br^-}{\rightleftharpoons} Sb_2Br_9^{3-} \overset{3Br^-}{\rightleftharpoons} 2SbBr_6^{3-}$$

or

$$2SbBr_3 \overset{Br^-}{\rightleftharpoons} Sb_2Br_7^- \overset{Br^-}{\rightleftharpoons} 2SbBr_4^-(Sb_2Br_8^{2-}?) \overset{4Br^-}{\rightleftharpoons} 2SbBr_6^{3-}$$

To ascertain which of these two reaction schemes is the more realistic, detailed, careful Raman measurements would be required together with conductivity and solubility studies.

The Raman spectrum assigned to the $SbBr_6^{3-}$ species in CH_2Cl_2 is rather unusual. It bears little resemblance to the vibrational spectra measured from solid state studies of bromoantimonate(III) complexes [6], which implies the presence of a completely different kind of distortion from the regular octahedral arrangement for the anion in this solution. In this respect the suggestion of C_{3v} symmetry made by Adams and Downs [5] seems particularly attractive. Under these circumstances the $SbBr_6^{3-}$ anion would be expected to possess a distorted octahedral structure with three short bonds opposite three long bonds.

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