75. *Raman Effect and Solvent Extraction. Part III.*[1] *Spectra of the Trichlorostannite and Tribromostannite Ions.*

By L. A. WOODWARD and M. J. TAYLOR.

An ether extract from a solution of stannous chloride containing hydrochloric acid gives a Raman spectrum which is attributed to the pyramidal trichlorostannite ion $SnCl_3^-$ ($\nu_1 = 297$ cm.$^{-1}$, strong, polarized; $\nu_2 = 128$ cm.$^{-1}$, weak, polarized; $\nu_3 = 256$ cm.$^{-1}$, medium, depolarized; $\nu_4 = 103$ cm.$^{-1}$, medium, depolarized). An extract from a solution of stannous bromide containing hydrobromic acid gives an analogous Raman spectrum which is attributed to the pyramidal tribromostannite ion $SnBr_3^-$ ($\nu_1 = 211$ cm.$^{-1}$, strong, polarized; $\nu_2 = 83$ cm.$^{-1}$, medium, polarized; $\nu_3 = 181$ cm.$^{-1}$, medium, depolarized; $\nu_4 = 65$ cm.$^{-1}$, medium, depolarized). The spectra of the aqueous solutions before extraction show that $SnCl_3^-$ and $SnBr_3^-$ ions are not the predominant complexes present.

AQUEOUS solutions of stannous chloride in hydrochloric acid and stannous bromide in hydrobromic acid have been shown [2-5] to give Raman spectra consisting of broad and diffuse " lines ". These were thought to indicate the presence of $SnCl_3^-$ and $SnBr_3^-$ ions; but the indefinite nature of the spectra suggests rather that the solutions contain mixtures of different complexes in equilibrium with one another. The situation is thus similar to that for acid solutions of indium chloride and bromide.[1] These likewise showed only indefinite Raman features; but extraction with organic solvents gave sharp spectra attributable to the single complex anions $InCl_4^-$ and $InBr_4^-$. The present paper reports similar work with acid stannous halide solutions, ether extracts from which are found to show distinct line spectra attributable with confidence to the single complex ions $SnCl_3^-$ and $SnBr_3^-$.

Stannous Chloride System.—The Raman spectrum of a solution containing 2M-stannous chloride and 6M-hydrochloric acid was found to consist of three broad and diffuse features

[1] Part I, *J.,* 1955, 1699; Part II, *J.,* 1960, 4473.
[2] Volkringer, Tchakirian, and Freymann, *Compt. rend.,* 1934, **199,** 292.
[3] Tchakirian and Volkringer, *Compt. rend.,* 1935, **200,** 1758.
[4] Delwaulle and François, *Compt. rend.,* 1940, **211,** 65.
[5] Delwaulle and François, *Compt. rend.,* 1941, **212,** 761.

centred respectively at ~113, 225, and 272 cm.$^{-1}$. This confirms the observations of the earlier workers. Volkringer, Tchakirian, and Freymann [3] gave the positions of the diffuse features as 112 (very broad), 218, and 265 cm.$^{-1}$. Delwaulle and François [4] gave 120 (broad, possibly double), 220, and 275 cm.$^{-1}$, and noted (in agreement with our own observation) that the " line " of highest frequency is polarized.

It is known that stannous chloride can be extracted from aqueous hydrochloric acid solution into diethyl ether.[6] The clear colourless extract obtained by shaking the above solution with an equal volume of ether gave a Raman spectrum which differed strikingly from that of the aqueous solution from which it was prepared. In addition to lines of the solvent, it showed four Raman lines due to the solute, all notably distinct and well-defined as compared with the diffuse features of the original aqueous solution. Table 1 gives the Raman frequencies, the estimated intensities, etc., of the lines, and their states of polarization.

TABLE 1.

Raman spectrum of stannous chloride extract.

$\Delta\nu$ (cm.$^{-1}$)	103	128	256	297
Intensity, etc.	Medium, broad	Weak, sharp	Medium, broad	Strong, sharp
Polarization	Depolarized	Polarized	Depolarized	Polarized

Stannous Bromide System.—The Raman spectrum of an aqueous solution containing 1·5M-stannous bromide and 4M-hydrobromic acid was found to consist of three broad and diffuse features centred at approximately 80, 140, and 200 cm.$^{-1}$. The spectrum was even less distinct than that of the aqueous solution of stannous chloride (see above). On account of the yellow colour the spectrum was excited by the green mercury line at 5461 Å instead of the usual blue mercury line at 4358 Å. In view of the diffuse character of the spectrum and the likelihood that the positions of the Raman features will depend to some extent upon the concentrations of stannous bromide and hydrobromic acid, our findings are in reasonable agreement with those of the earlier workers. Tchakirian and Volkringer [3] gave the positions of the features as 60—90 (broad), 160, and 180 cm.$^{-1}$. Delwaulle and François [5] gave 65—93 (broad), 155, and 181 cm.$^{-1}$, and noted (in agreement with our own observation) that the " line " of highest frequency is polarized.

It has been shown [7] that stannous bromide is readily extractable by diethyl ether from acid aqueous solutions. The extract obtained by shaking the above solution with an equal volume of ether was much paler than the original aqueous solution, and its Raman spectrum was obtained without difficulty by using excitation with the blue mercury line 4358 Å. As for stannous chloride, the spectrum of the extract was remarkably clear and well-defined, compared with that of the aqueous solution from which it was prepared. Like that of the stannous chloride extract, it consisted of four lines (see Table 2).

TABLE 2.

Raman spectrum of stannous bromide extract.

$\Delta\nu$ (cm.$^{-1}$)	65	83	181	211
Intensity, etc.	Medium	Medium, sharp	Medium, broad	Strong, sharp
Polarization	Depolarized	Polarized	Depolarized	Polarized

Discussion of Spectra.—We shall consider first the relatively distinct and well-defined Raman spectra of the ether extracts. The contrast with the diffuse and ill-defined spectra of the aqueous solutions suggests strongly that, although the original aqueous solutions contained different complexes in equilibrium, extraction of the metal involves in each case passage of only one complex species into the ether phase. Moreover, the " pattern " of the observed extract spectra, which is the same for both chloride and bromide, provides

[6] Morrison and Freiser, " Solvent Extraction in Analytical Chemistry," John Wiley and Sons, New York, 1957, p. 129.

[7] Bock, Kusche, and Bock, *Z. analyt. Chem.*, 1953, **138**, 167.

very strong evidence that the single species involved is, respectively, the trichlorostannite ion $SnCl_3^-$ and the tribromostannite ion $SnBr_3^-$.

The spectrum of each extract consists of four lines, two of which (including that of highest frequency) are polarized. This is exactly the type of Raman spectrum expected, according to the rules of selection and polarization, for a species of the type MX_3 of pyramidal shape (point group C_{3v}). The ions $SnCl_3^-$ and $SnBr_3^-$, in which the metal atom has a valency octet including one unshared electron pair, are expected to have this shape. Indeed, no other complexes that might reasonably be postulated would give rise to spectra of the type observed.

The ions $SnCl_3^-$ and $SnBr_3^-$ are isoelectronic with the pyramidal molecules $SbCl_3$ and $SbBr_3$, respectively. The comparison of the Raman spectra of the isoelectronic pairs given in Table 3 provides strong support for our conclusion that the species extracted into

TABLE 3.

Vibrational frequencies (cm.$^{-1}$) of isoelectronic species MCl_3 and MBr_3.

	$\nu_1 (a_1)$	$\nu_2 (a_1)$	$\nu_3 (e)$	$\nu_4 (e)$	Ref.
$SnCl_3^-$	297	128	256	103	Present work
$SbCl_3$	360	165	320	134	8
$\nu(SnCl_3^-)/\nu(SbCl_3)$	0·82	0·78	0·80	0·77	
$SnBr_3^-$......................................	211	83	181	65	Present work
$SbBr_3$	254	101	245	81	9
$\nu(SnBr_3^-)/\nu(SbBr_3)$..........................	0·83	0·82	0·74	0·80	

ether is the trihalogenostannite ion. In each pair the spectra of the ion and the iso-electronic molecule are analogous, each of the frequencies of SbX_3 being greater than the corresponding one of SnX_3^-. This is in accordance with expectation, since passage from SnX_3^- to SbX_3 is associated with an increase of the nuclear charge of the metal atom, causing a tightening of the bonds to the halogen atoms.

The existence of the trichlorostannite ion is confirmed in a recent note by Grdenić and Kemenar,[10] published after the conclusion of the present work. They identified this ion in the crystal of the compound usually written as K_2SnCl_4,H_2O. A new analysis of the X-ray data shows that the crystal contains the pyramidal $SnCl_3^-$ unit, and that the compound is therefore better formulated as $KCl,KSnCl_3,H_2O$. They had previously shown [11] the presence in crystalline stannous chloride dihydrate of the analogous pyramidal complex $Sn(H_2O)Cl_2$, in which the tin atom likewise has a valency octet containing one unshared electron pair.

The diffuseness of the Raman spectra of the aqueous solutions before extraction makes it difficult to draw definite conclusions from them. Doubtless the solutions contain different complexes in equilibrium with one another. We note that in each case the diffuse feature of highest frequency is centred at a value considerably lower than ν_1 of SnX_3^-, which appears as a very intense, sharp line in the spectra of the extracts. Hence, on the reasonable assumption that (as has been verified [1] for $GaCl_4^-$) the frequency of SnX_3^- is not subject to any considerable effect of environment, we conclude that the concentration of SnX_3^- ions in the aqueous solution must be small. No doubt in each case the polarized Raman feature of highest frequency in the aqueous solution, like ν_1 of SnX_3^-, is essentially associated with symmetrical metal–halogen stretching; and since additional co-ordination on to the metal atom is expected to lower the frequency of this type of vibration, it is probable that the aqueous solutions contain higher complexes than SnX_3^-, such as SnX_4^{2-}, etc.

Nevertheless, in the ether extraction it is only (or at least predominantly) SnX_3^- that

[8] Herzberg, "Infra-red and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, 1945, p. 164.
[9] Evans, *J. Mol. Spectroscopy*, 1960, **4**, 435.
[10] Grdenić and Kamenar, *Proc. Chem. Soc.*, 1961, 304.
[11] Grdenić and Kamenar, *Proc. Chem. Soc.*, 1960, 312.

P

passes into the organic phase—no doubt as ion pairs $H^+SnX_3^-$, in which the hydrogen ion is probably solvated. The process is thus similar to the extraction of tervalent indium and iron from acid halide solutions, where the Raman evidence [1] has shown that ion pairs of the type $H^+MX_4^-$ are involved. It appears to be a characteristic of ether extractions from acid halide solutions that the singly charged complex anion of the metal passes much more readily into the organic phase than do complex anions of higher charge.

Experimental.—Preparation of solutions and extracts. The aqueous solutions were prepared by dissolving weighed amounts of " AnalaR " stannous chloride and pure powdered stannous bromide in the appropriate volumes of the corresponding pure concentrated halogen acids of known concentration. The extracts were prepared by shaking the aqueous solution (5 ml.) at room temperature with pure peroxide-free diethyl ether (5 ml.). The extract of stannous chloride had a volume of ~6 ml., to be compared with ~4 ml. for the aqueous phase in equilibrium with it. The volume of the bromide extract was ~5·5 ml., to be compared with 4·5 ml. for the aqueous phase.

Raman spectra. These were excited by a Toronto-type mercury-arc source, with a sample volume of about 5 ml. For all the spectra except that of the aqueous stannous bromide the exciting line was Hg 4358 Å (blue). The yellow colour of the aqueous bromide solution made it more convenient to use the green mercury line (5461 Å) in this case. The spectra were recorded photographically, by means of a Hilger E 612 two-prism spectrograph with f/5·6 camera (dispersion about 95 cm.$^{-1}$ per mm. in the region of lines excited by Hg 4358 Å and about 160 cm.$^{-1}$ per mm. in the region of lines excited by Hg 5461 Å). The plates used were Kodak Special Scientific Oa, G, and for each solution a number of spectra were photographed with a wide range of exposure times. Frequencies were determined in the usual manner with an iron-arc spectrum as standard. The limits of error are about ± 2 cm.$^{-1}$ for well-defined lines. The location of the centres of the diffuse features of the aqueous solutions is necessarily less precise. States of polarization were determined qualitatively by the method of polarized incident light, successive spectra being photographed with the same exposure time but with suitably oriented Polaroid cylinders surrounding the sample tube.

THE INORGANIC CHEMISTRY LABORATORY,
SOUTH PARKS ROAD, OXFORD.