The values for $\sigma(m_H)$, $\sigma(h)$, and $\sigma(m_b)$ are obtained from the observables by application of the propagation of error principle. An analysis of this kind was made on selected data at 60° covering the range of $\bar{n}$ and m_b. In a given run $\sigma^2(F)$ was found to vary no more than 50% in going from an $\bar{n}$ of 0.1 to 1.0 and it was found in different runs to depend largely on the ratio $m_{H,0}/m_b$ (initial free acidity to the total beryllium concentration) which varied between about 0.5 and 1.3. The following expression represents this dependence

$$\sigma(F) = 0.00125 + 0.0075(m_{H,0}/m_b) \qquad (12)$$

Equation 12 was used to weight all of the data at 60 and 25° and the calculation for the best scheme for each value of x in Figure 3 was repeated. Essentially the same relative relationship between schemes was obtained as is shown in Figure 3. The agreement factor calculated using W from eq 9 indicates the agreement within some number of units of standard error. For scheme I (Table III) the agreement factor at 60° was 1.1 and at 25°, using the same estimates of error, it was 2.1. This probably indicates that the error at 25° was underestimated. Nevertheless, agreement within a factor of 2 of the estimated error (0.01 unit in $\bar{n}$) is considered good and, therefore, one has no justification for adding additional complexes to the three-species schemes to attempt further minimization of F.

Formation quotients calculated from weighted data at these two temperatures did not differ from the previous values by more than σ in most cases and never by more than 2σ. Thus, the approximation of equal weighting, which is generally made, is found to lead to very minor errors in this case and probably need be examined in detail only in cases where marginal effects might be expected to alter conclusions from the data.

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Raman Study of Chloride and Bromide Complexes of Bismuth(III)[1]

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Raman intensity measurements were made on aqueous solutions containing various ratios of chloride to bismuth. The species $BiCl_4^-$, $BiCl_5^{2-}$, and $BiCl_6^{3-}$ were identified, and their frequencies were determined. In addition, species containing three, two, and possibly one Cl^- per Bi(III) were found. Experiments with bismuth bromide solutions showed that $BiBr_6^{3-}$ is the highest species formed, and not $BiBr_8^{5-}$ as previously postulated. Raman spectra of crystalline solids containing $BiCl_4^-$, $BiCl_5^{2-}$, $BiCl_6^{3-}$, and $BiBr_6^{3-}$ were recorded for comparison. No evidence was found for either hydrolytic hydroxide bridging or halide bridging in solution. A weak polarized band at *ca.* 390 cm^{-1} can be assigned to the symmetric bismuth–water stretching motion. The ClO_4^- ν_3 band at 1120 cm^{-1} reveals a shoulder at 1040 cm^{-1} in dilute bismuth perchlorate solutions. This might be assigned to a BiO^+ species with considerable uncertainty. Structural considerations are presented for all of the complex bismuth halide species identified.

Introduction

Aqueous bismuth(III) chloride and bromide complexes have been the subject of considerable investigation during the past 10 years. From spectrophotometric studies, Newman and Hume[3] established the existence of species $BiCl_n^{3-n}$, where n = 1–5. Ahrland and Grenthe[4] found potentiometrically that n assumes values 1–6 for both $BiCl_n^{3-n}$ and $BiBr_n^{3-n}$ and that the fifth complex has an exceptionally wide range of existence. Haight and co-workers[5] have more recently used solubility methods to investigate the bismuth bromide system and the high-ligand-number region of the chloride system. They found n = 1, 2, 4, 6, and 8 for $BiBr_n^{3-n}$ and n = 4 and 6 for the two $BiCl_n^{3-n}$ species involved in the highest equilibrium in chloride solutions. Their data indicate that complex species with n = 3 or 5 are either absent or present only in extremely low concentration, in conflict with the results of the previous workers. The possibility of eight coordination in the highest bromide complex is a further subject for debate. It was with the objects in mind of resolving these questions and extending the current state of knowledge to more concentrated solutions that the present Raman study was initiated.

Compared with most other common techniques used for the characterization of aqueous complex ions, Raman spectroscopy is considerably more direct and reliable. By both treating solution spectra as quantitatively as possible and using spectra of the appropriate solids for comparison, it is possible to determine the stoichiometry and structure of the predominant solution species. Where such studies have been conducted in other halide systems, it has frequently been

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[1] Sponsored by a research grant from the Office of Saline Water, U. S. Department of the Interior.

[2] Financially supported by a National Science Foundation Predoctoral Fellowship, 1966–1967.

[3] L. Newman and D. N. Hume, *J. Am. Chem. Soc.*, **79**, 4576 (1957).

[4] S. Ahrland and I. Grenthe, *Acta Chem. Scand.*, **11**, 1111 (1957).

[5] (a) G. P. Haight, Jr., C. H. Springer, and O. J. Heilmann, *Inorg. Chem.*, **3**, 195 (1964); (b) J. R. Preer and G. P. Haight, Jr., *ibid.*, **5**, 656 (1966).

found that a stepwise series of complex ions is not present.[6-9] Thus, an additional motivation for the present study is to see whether or not an entire stepwise series is formed for the complex halides of Bi(III). In these systems, only meager photographically recorded Raman data are available.[10-12] They are only qualitative in nature and no species have been identified or frequencies assigned. Although numerous crystalline halobismuthates have been prepared,[13-16] their vibrational spectra have never been recorded. Except for the anion $BiCl_5^{2-}$, which was shown to be a distorted octahedron in "bismuth monochloride" ($BiCl_{1.167}$),[17] and $BiCl_6^{3-}$, which was found to be octahedral in $Co(NH_3)_6BiCl_6$,[18] their structures have never been definitively established by X-ray diffraction.

Experimental Section

Solutions.—Bismuth(III) chloride monohydrate (Mallinckrodt) and anhydrous bismuth(III) chloride (J. T. Baker) and bromide (Alfa) were reagent grade, used without further purification. To obtain ratios of $[Cl^-]/[Bi(III)]$ less than 3/1, a solution of reagent bismuth oxide (Fisher) or basic carbonate (J. T. Baker) in 9.6 M $HClO_4$ was added to a 0.55 M solution of bismuth chloride in 8.9 M $HClO_4$. Ratios greater than 3/1 were obtained by adding hydrochloric acid to the last-mentioned solution. All of the bromide solutions studied were prepared in an analogous manner, although $[Br^-]/[Bi(III)]$ ratios below 5/1 were difficult to study systematically because of the insolubility of $BiBr_3$ in $HClO_4$. In both the chloride and the bromide solutions, the eventual precipitation of the bismuth oxyhalide prevented the preparation of low [halide]/[Bi(III)] ratios (below ~2.5/1) using the above methods. In none of the solutions investigated was any decomposition detected with time. Each was filtered through a fine glass frit before its Raman spectrum was recorded. The solutions were analyzed gravimetrically for bismuth as the oxyhalide and for halogen as AgCl or AgBr. They were not analyzed for perchlorate (the Raman intensity standard), since only its relative concentration was necessary in all cases, and this was known from the fact that solutions were prepared by quantitative dilution. For the nonaqueous solutions, anhydrous methanol (dried over calcium oxide), 1-butanol (dried over barium oxide), and reagent acetone were used.

Solids.—The solid substituted ammonium chlorobismuthates were prepared according to Remy and Pellens,[13] by adding a solution of the appropriate ammonium chloride to a solution of $BiCl_3$ in HCl and recrystallizing the resulting salt from 3 M HCl. The hydrazinium halobismuthates, $(N_2H_5)_3BiCl_6$ and $(N_2H_5)_3BiBr_6$, were made according to Pugh,[14] as was the dimethylketazinium salt of $BiCl_4^-$, $C_6H_{13}N_2BiCl_4$.[15] All crystalline solids were handled in a nitrogen-filled glove bag during sample preparation.

Raman Spectra.—The spectra were measured on a Cary Model 81 Raman spectrophotometer, using the 4358-A mercury line for excitation of the colorless chloride solutions and solids and the 5461-A mercury line (green) for the yellow bromide solutions and solid, which had zero absorbance at this wavelength. The 5461-A mercury line was isolated by surrounding the sample with a green filter solution containing $CuSO_4$, $Cu(NO_3)_2$, $K_2Cr_2O_7$, and Pr_2O_3 in such proportions as to give maximum transmittance (*ca.* 30%) at 548 mμ. Whereas the ν_1 band of ClO_4^- at 933 cm^{-1} was used as the internal intensity standard in all of the chloride solutions, it could not be used for the bromide experiments because of intense mercury lines which interfered at 5771 A ($\Delta\nu = 980\ cm^{-1}$) and 5792 A ($\Delta\nu = 1043\ cm^{-1}$). Instead, the ν_2 band of ClO_4^- at 460 cm^{-1} served as intensity standard for the bromide study, in which the estimated uncertainty in intensity measurements was about 10% owing to the weakness of this particular ClO_4^- vibrational mode. Raman spectra were recorded at the ambient lamp compartment temperature, 43°. Polarization measurements were made by surrounding the sample tube with Polaroid sheets which had been calibrated using $CHCl_3$, CCl_4, and C_6H_6.[19] Solid spectra were obtained using either a straight 14-mm glass tube or the conical sample holder described in the literature.[20]

Results

Chloride Solutions.—A Raman spectrum characteristic of aqueous bismuth chloride solutions is reproduced in Figure 1, along with the resolved component bands lowered to a horizontal background. In this specific case R (the formal ratio $[Cl^-]/[Bi(III)]$) equals 2.6 ($[Bi(III)] = 0.58\ M$, $[H^+] = 8.8\ M$). Solutions with R greater than 2.6 yield spectra of the same general appearance, consisting of an intense polarized band at highest frequency with a weaker depolarized shoulder on its low-frequency side, in addition to a depolarized band at a still lower frequency which, in general, is relatively much weaker than in the $R = 2.6$ spectrum. Judging from relative intensity and position, the first two lines correspond to symmetric and asymmetric Bi–Cl stretching motions of complex $BiCl_n^{3-n}(aq)$ species, respectively, while the third line is due to excitation of bending vibrational modes. Figure 2 shows the observed lowering in frequency of the two higher lines (ν_p and ν_{dp}) as R is increased. A simultaneous, though less abrupt, lowering is seen in the bending region from about 121 to 110 cm^{-1} as R is increased from 2.6 to 20.0.

Because of its position as a weak shoulder on the Rayleigh line, the Raman band in the bending region was neither resolved nor studied quantitatively. However, several methods of graphically resolving the high-frequency envelope were used in order to learn as much as possible about the strong polarized component. By applying each method consistently to all solution spectra, the results were found to be essentially independent of the chosen resolution technique. The final method of choice involved first subtracting graphically the large symmetric polarized peak from the overall envelope, thus leaving a small asymmetric band which could itself be resolved into two or three components in certain favorable cases. This was the method used in Figure 1. The result is an asymmetric depolarized band with the broad wing on the low-frequency side through $R = 4$ or 4.5, when it becomes symmetric. In solutions of $4.5 < R < 8.5$, the broad

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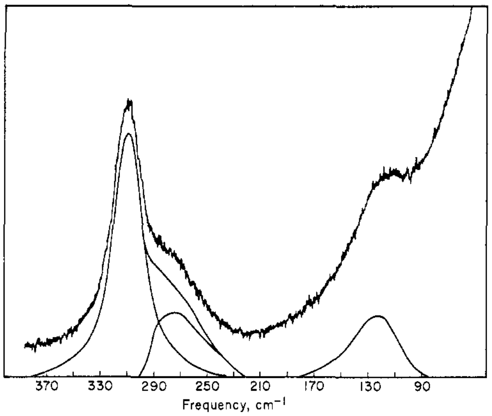

Figure 1.—Raman spectrum of $R = 2.6$ bismuth chloride solution ($[Bi(III)] = 0.58\ M$, $[Cl^-] = 1.50\ M$, $[H^+] = 8.8\ M$), with resolved features lowered to horizontal background. Cary Model 81, RD 4, lamp current 15 amp, single-slit width 9 cm^{-1}, scan speed 0.25 cm^{-1}/sec, gain 100.

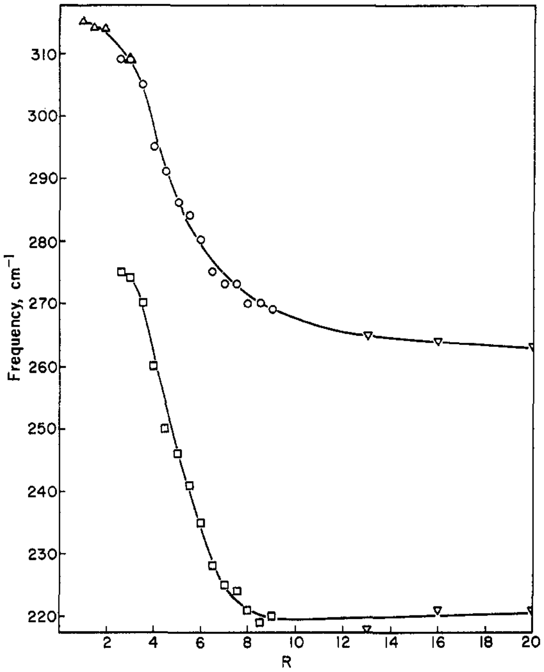

Figure 2.—Frequencies of polarized and depolarized bands vs. R in the chloride system stretching region: ○, polarized band in Job analysis solutions of constant total $[Bi(III)] + [Cl^-] = 2.08\ M$, ($[Bi(III)] = 0.58$–$0.21\ M$, $[Cl^-] = 1.50$–$1.87\ M$, $[H^+] = 8.8$–$4.6\ M$); □, depolarized band in same Job solutions of constant total $[Bi(III)] + [Cl^-] = 2.08\ M$; △, LiCl + BiOCl + $HClO_4$ solutions ($[Bi(III)] = 0.027\ M$, $[H^+] = 9.6\ M$); ▽, $[Bi(III)] = 0.30\ M$, $[H^+] = 1.8$–$6.0\ M$.

wing moves to the high-frequency side, and above $R = 8.5$ the band is again completely symmetric. Depolarization ratios, ρ, range from 0.03 to 0.09 for the polarized peak and from 0.73 ($R = 3.0$) to 0.42 ($R = 4.5$) to a final value of 0.86 ($\rho = {}^6/_7$) above $R = 7.5$ for the resolved shoulder. Although the latter peak is in actuality depolarized, it often has $\rho < {}^6/_7$ probably because the polarized band is not perfectly symmetric, as assumed above, owing to the presence of more than one species.

Several other general features of the solution spectra are worthy of note. As Figure 3 shows, there is a remarkable initial broadening of $\omega_{1/2}$ (width at half-height) of the polarized band as R is increased, followed by a narrowing which approaches the limiting value $\omega_{1/2} = 41$ cm^{-1} for large R. The two minima at $R = 3.0$ and $R = 4.5$ are of further significance in that they indicate the probable short-range predominance of a single complex species in solutions with these R values. This spectral behavior is accompanied by broadening of the resolved depolarized band to a maximum of *ca.* 55 cm^{-1} at $R = 4.5$, with a subsequent sharpening as R increases further. Figure 4 indicates the R dependence of the ratio of integrated intensity of polarized band to depolarized band in the stretching region. Each $BiCl_n^{3-n}(aq)$ species which exhibits both symmetric and asymmetric Raman-active stretching vibrations should have a characteristic value for such an intensity ratio. It should be true that the shape of the curve in Figure 4 can be related to the presence of several such species. A broad minimum is apparent near $R = 4$ and there is leveling off at higher R.

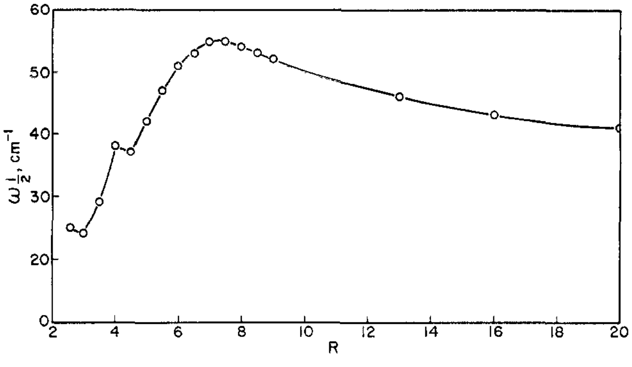

Figure 3.—Width at half-height, $\omega_{1/2}$ (cm^{-1}), of resolved polarized band in bismuth chloride solutions used in Job analysis (same total and range of concentrations as in Figure 2) as a function of R.

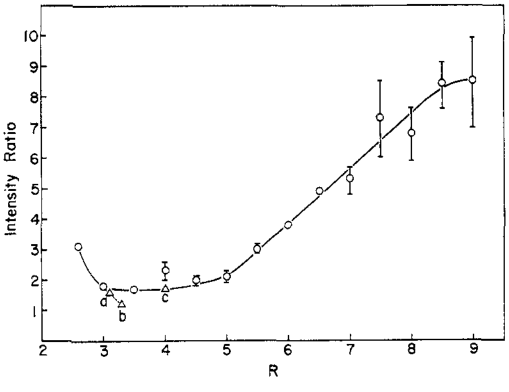

Figure 4.—Intensity ratio (integrated areas) of resolved polarized band to depolarized band vs. R in the chloride system: ○, Job analysis solutions (same total and range of concentration as in Figure 2); a, 0.13 M $BiCl_3$ in methanol; b, 0.13 M $BiCl_3$ in 1-butanol; c, *ca.* 0.1 M $C_6H_{13}N_2BiCl_4$ in acetone.

Two series of experiments were performed in an attempt to establish the identity of $BiCl_n^{3-n}(aq)$ species giving rise to the spectral characteristics mentioned above. The first was designed after the Job method of continuous variations[21] and made use of 14 solutions

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(21) P. Job, *Ann. Chim.* (Paris), [10] 9, 113 (1928).

containing a fixed sum of stoichiometric concentrations ([Bi(III)] + [Cl$^-$] = 2.08 M), but with variation in formal ratio of ligand to metal (R = 2.6–9.0). Band heights were obtained at 5- or 10-cm^{-1} frequency intervals for both polarized and depolarized bands in the stretching region. They were normalized to a known concentration of internal ClO_4^- standard. Our use of the ν_1 band of ClO_4^- as intensity standard in these solutions containing as much as 9 M $HClO_4$ is justified by the work of Covington, *et al.*,[22] who performed intensity measurements on precisely this band to show that $HClO_4$ is essentially completely dissociated up to 10 M. The results of the present Job analysis are shown in Table I, where the value of R at which the normalized band height maximizes, R_{max}, is listed beside the corresponding selected frequency.

TABLE I

JOB ANALYSIS OF BISMUTH CHLORIDE SOLUTIONS

[Bi(III)] + [Cl$^-$] = 2.08 M

Freq of polarized band, cm^{-1}	R_{max}[a]	Freq of depolarized band, cm^{-1}	R_{max}[a]
320	<3	300	*Ca.* 3
310	3.0	280	3.0
305	3.0	270	3.0
300	3.5	260	3.0, 4.0[b]
295	4.0	250	4.0
290	4.0	240	4.5
280	5.0	230	4.5
270	6.0	220	*Ca.* 5
260	*Ca.* 7	210	*Ca.* 7

[a] Formal ratio at which normalized band height maximizes, in experiments with R differing by units of 0.5. [b] 260 cm^{-1} intensity has a double maximum with a shallow minimum at 3.5.

In an attempt to investigate the equilibrium between the two highest species and perhaps even detect an isosbestic point, a series of seven solutions was prepared with constant stoichiometric metal concentration ([Bi(III)] = 0.30 M), but varied formal ratio (R = 6.0–20.0). In Figure 5 are reproduced the resolved polarized bands so obtained (normalized to known ClO_4^- concentration). There is clearly an isosbestic point at 276 cm^{-1} involving spectra of solutions with R = 8.0–20.0. Spectra obtained from R = 6.0 and 7.0 solutions do not pass through this common point.

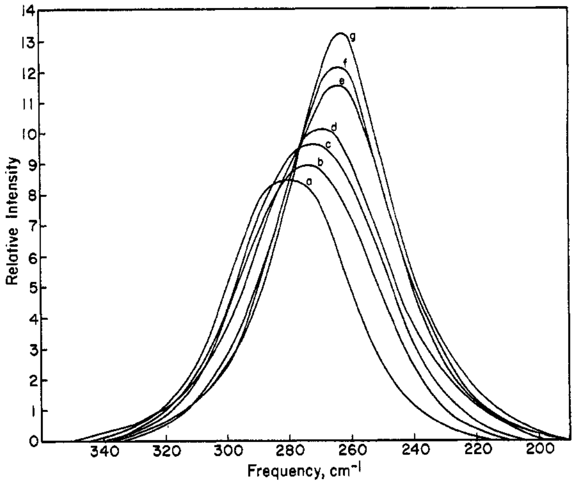

Figure 5.—Resolved polarized band (normalized to known ClO_4^- concentration) in chloride solutions of [Bi(III)] = 0.30 M, [H$^+$] = 1.8–6.0 M, and R values of: a, 6.0; b, 7.0; c, 8.0; d, 9.0; e, 13.0; f, 16.0; g, 20.0.

The lowest formal ratio mentioned thus far has been R = 2.6. This is hardly sufficiently low to permit the study of species containing fewer than three chlorides per bismuth, but the precipitation of BiOCl made such investigation exceedingly difficult. Since the spectra recorded for higher R demonstrate the generally strong Raman scattering ability of $BiCl_n^{3-n}$(aq), the spectrum was run of 9.5 M $HClO_4$ saturated with BiOCl (analyzed [Bi(III)] = 0.027 M), where R = 1.0, as well as the spectra of solutions having the same stoichiometric [Bi(III)] but prepared to be R = 1.5, 2.0, and 3.0 with added LiCl. The Bi–Cl stretching region is, not unexpectedly, very weak, but its intensity increases as R is raised. For R = 1.0, 1.5, and 2.0 the band is broad, symmetric, and polarized, whereas for R = 3.0 it is asymmetric and resembles the more concentrated R = 3.0 spectrum. The variation in frequency from 315 cm^{-1} (R = 1.0) to 309 cm^{-1} (R = 3.0) is included in Figure 2.

Two additional solutions were prepared in the hope of isolating the solvated trichloro species: (1) 0.13 M $BiCl_3$ in anhydrous methanol and (2) 0.13 M $BiCl_3$ in anhydrous 1-butanol. In the former R = 3.1 and in the latter R = 3.3, presumably owing to a small amount of hydrolytic precipitation of BiOCl. The polarized Bi–Cl stretching band is found at 305 cm^{-1} in methanol solution and at 302 cm^{-1} in 1-butanol, while the depolarized stretching band is at 268 and 264 cm^{-1}, respectively. Figure 4 includes the intensity ratio of polarized band to depolarized band for these nonaqueous solutions.

Raman lines which could be assigned to oxygen-containing complex bismuth species were searched for at great length. None of the bands which Maroni and Spiro[23] attribute to $Bi_6(OH)_{12}^{6+}$ could be found in the spectra of the solutions studied here, except when we examined concentrated bismuth perchlorate solutions prepared especially to approach their solution conditions. Only then did the polarized 177-cm^{-1} band due to hydrolytic hexamer begin to appear. In the more dilute, strongly acidic bismuth perchlorate solutions ([Bi(III)] $\lesssim$ 0.8 M, [$HClO_4$] = 9.6 M) which contain insufficient hexamer to yield its spectrum, a weak polarized band is observed at *ca.* 390 cm^{-1} under the low-frequency wing of the 460-cm^{-1} ClO_4^- band. This is located in the metal–hydrate symmetric stretching region.[24] In none of the chloride-containing solution spectra can this band be seen, owing either to its absence or merely to the proximity of the intense Bi–Cl symmetric stretching mode in addition to the ClO_4^- band.

Although the four lines typical of free perchlorate

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[22] A. K. Covington, M. J. Tait, and W. F. K. Wynne-Jones, *Proc. Roy. Soc.* (London), **A286**, 235 (1965).

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strictly maintain their position in the dilute bismuth perchlorate solutions (as they do in all others, as well), a definite shoulder, probably polarized, is evident at *ca.* 1040 cm^{-1} on the low-frequency side of the 1120-cm^{-1} (ν_3) band. The other degenerate modes retain an unsplit appearance. The height of the shoulder at 1040 cm^{-1} relative to the 1120-cm^{-1} ClO_4^- band increases as the Bi(III) concentration is increased in solutions of constant $HClO_4$ formality. A corresponding increase in width at half-height of the entire envelope is noted. Even as the bands due to hexamer begin to appear, the shoulder persists. Its position at 1040 cm^{-1} is in the region characteristic of metal oxocations of the form $M = O^{x+}$.[25]

Chloride Solids.—Despite the lack of X-ray structural data on crystalline halobismuthates, a number of the chloro salts were prepared and their Raman spectra recorded for comparison with the solution spectra. Table II lists the compounds and gives the observed frequencies. In some cases the low-frequency bending region is featureless owing to spectral recording difficulties. An additional experiment was prompted by the report[15] that $C_6N_{13}N_2BiCl_4$ acts as a 1:1 electrolytic conductor in solutions of ketones. Such a solution was prepared in acetone (*ca.* 0.1 *M* in Bi(III)); its Raman spectrum shows the usual solution envelope with ν_p 290 cm^{-1}, ν_{dp} 255 cm^{-1}, and an intensity ratio of polarized band to depolarized band equal to 1.7.

Table II

Raman Spectra[a] of Solid Chlorobismuthates

Compound	Obsd freq, cm^{-1}, due to chloroanion (intensity[b])
$C_6H_{13}N_2BiCl_4$[c]	290 (s, sh), 267 (m, sh), 220 (w, b), 95 (w), 80 (w)
$(C_2H_5NH_3)_2BiCl_5$	276 (s, sh), 228 (m, sh), *ca.* 100 (vw)
$(C_2H_5NH_3)_3BiCl_6$	256 (s, sh), 213 (w, sh)
$(N_2H_5)_3BiCl_6$	260 (s, sh), 215 (w, b), *ca.* 100 (w)

[a] Cary Model 81, RD 4, lamp current 15 amp, single-slit width 6 cm^{-1}, average gain 1.5 × 100. [b] s, strong; m, medium; w, weak; sh, sharp; b, broad; v, very. [c] The analogous tetrachloroantimonate(III) was prepared to separate Raman shifts due to cation.

Bromide Solutions and Solid.—Because the higher complex $BiBr_n^{3-n}$(aq) species are of most immediate interest and because of solubility problems, formal ratios of $[Br^-]/[Bi(III)]$ examined are within the limited range *R* = 5.1–14.0. All of the yellow bismuth bromide solutions give Raman spectra with general appearance and behavior very similar to those of the chloride solutions. Spectral resolution was achieved in an identical manner. The high-frequency Bi–Br stretching region contains the same two bands, an intense polarized one at higher frequency with a weak depolarized shoulder on the low-frequency side. These two lines are separated by only 24 cm^{-1}, compared to 35–50 cm^{-1} in the chloride solution spectra. The bending region also contains a depolarized band of medium intensity. As *R* is increased above 5.1 (for $[Bi(III)] + [Br^-] = 3.61$ *M*, $[H^+] = 5.5$ *M*), the polarized line moves smoothly from 180 to 161 cm^{-1}, the high-frequency depolarized line from *ca.* 156 to 137 cm^{-1}, and the low-frequency depolarized band from 65 to 57 cm^{-1}. The limiting frequencies (161, 137, and 57 cm^{-1}) are reached at $R = 7.5$ (for $[Bi(III)] + [Br^-] = 3.61$ *M*, $[H^+] = 5.5$ *M*) and maintained at all higher *R* values. At the same time, the width at half-height of the polarized band decreases from *ca.* 52 cm^{-1} at $R = 5.1$ to a limiting value of 37 cm^{-1} at $R = 8.5$.

Two series of experiments were performed. The first followed the Job method and involved 11 solutions in which the fixed sum of stoichiometric concentrations $[Bi(III)] + [Br^-]$ equaled 3.61 *M*, with variation in *R* from 5.1 to 10.0 ($[H^+] = 5.5$ *M*). Normalized band heights were taken at 10-cm^{-1} intervals for the two strongest spectral features, these being the resolved polarized stretching and depolarized bending bands. The normalized heights at 200, 190, 180, and 170 cm^{-1} maximize at some *R* less than 5.1, whereas those at 160, 150, and 140 cm^{-1} maximize at $R = 6.0$–6.5. Similarly, the normalized height at 65 cm^{-1} peaks at some *R* less than 5.1, while that at 55 cm^{-1} peaks at $R \cong 6.0$.

A second set of experiments made use of seven solutions in which the stoichiometric Bi(III) concentration was maintained at 0.36 *M* and *R* varied over the range 5.5–14.0 ($[H^+] = 4.4$–7.4 *M*). As in the case of the chloride solutions, the normalized spectra increase in intensity as *R* is raised, but no definite isosbestic point is apparent in the bromide system. Instead, what may be termed an "isosbestic region" is in evidence over the frequency range 166–173 cm^{-1}. This might be due partially to the error resulting from poor spectral quality of the internal intensity standard (460-cm^{-1} band of ClO_4^-) when the 5461-A mercury line is used for excitation, or it may indicate that, unlike the Cl^- case, more than two complexes are in significant equilibrium concentration.

The yellow crystalline solid $(N_2H_5)_3BiBr_6$ was prepared and its Raman spectrum recorded. Three lines are observed at 156 (s, sh), 133 (w, b), and 63 (m, b) cm^{-1} and are attributable to the $BiBr_6^{3-}$ anion.

Discussion

Chloride System.—From Figures 2–4 it is apparent that several $BiCl_n^{3-n}$(aq) species are contributing to the spectral behavior of the solutions. The marked fall in Bi–Cl stretching frequency with increasing *R* is a clear indication of the formation of higher complexes. A similar decrease in frequency is noted, for example, in the Raman spectra of aqueous thallium(III) chloride,[26] zinc bromide,[8] and zinc chloride[9] species as the ligand number about the central metal increases. Further evidence for the existence of more than one species is found in the variation in asymmetry of the depolarized stretching band. The gradual decrease to a limiting value at large *R* of $\omega_{1/2}$ of the polarized band corresponds to essentially complete formation of the highest complex. This species exhibits the three limiting frequencies 263, 220, and *ca.* 110 cm^{-1}. That

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(25) J. Selbin, *Angew. Chem. Intern. Ed. Engl.*, **5**, 712 (1966).

(26) T. G. Spiro, *Inorg. Chem.*, **4**, 731 (1965).

this aqueous complex is $BiCl_6^{3-}$ is shown most convincingly by the close correspondence between these frequencies and those of the solid $BiCl_6^{3-}$ anion, which average 258, 214, and *ca.* 100 cm^{-1} in the two salts examined. Small differences usually accompany change in phase from solution to solid.

The Job analysis (Table I) is consistent with this conclusion. In a system containing several successive equilibria, as the present one almost certainly does, the method of continuous variations can be expected to yield only an indication of the minimum number of species present. It does not necessarily give the corresponding stoichiometries unambiguously. In such a system, the normalized spectral band height due to the highest species is expected to maximize at a formal ratio slightly greater than that of the relevant stoichiometry.[27] This is borne out in Table I by $R_{max} \cong 7$ for the two lowest frequencies. The remaining task, then, is to verify the exact stoichiometry and probable frequencies for the species indicated by the Job analysis (of the polarized band) at $R_{max} = 5$ (280 cm^{-1}), 4 (*ca.* 293 cm^{-1}), 3 (*ca.* 307 cm^{-1}), and $R_{max} < 3$ (>310 cm^{-1}).

The isosbestic point observed at 276 cm^{-1} for R = 8.0–20.0 most likely arises from the equilibrium between $BiCl_6^{3-}$ and the next lower species. Solutions with $R = 6.0$ and 7.0 have additional interfering equilibria involving still lower species and therefore do not pass through this point. To decide whether the species (in addition to $BiCl_6^{3-}$) responsible for the isosbestic point is $BiCl_4^-$ or $BiCl_5^{2-}$, the following procedure was tried. From the known Raman line of $BiCl_4^-$ obtained in acetone solution of $C_6H_{13}N_2BiCl_4$ (and verified in aqueous solution of $R = 4.5$ where spectral comparison shows that the solution contains a preponderance of Bi(III) as $BiCl_4^-$) and that of $BiCl_6^{3-}$ obtained from the solutions of high [Cl^-], attempts were made to synthesize the Raman spectra of Figure 5 for the region R = 6–20. These attempts failed on three counts: (a) the line intensities observed for R = 6, 7, 8, 9, 13, and 16 are all found to be less than calculated; (b) the isosbestic point would occur at 282 cm^{-1} and not at the observed 276 cm^{-1}; (c) the isosbestic point would occur at $R < 6$ and not in the region observed of $R > 8$. If, however, one postulates the existence of the species $BiCl_5^{2-}$, having a Raman frequency near 280 cm^{-1}, as predicted from the observed spectrum of solid $(C_2H_5NH_3)_2BiCl_5$, then all of the observed spectra can be explained quantitatively, within the uncertainty of the resolved curves plotted. Furthermore, on the basis of the existence in solution of $BiCl_5^{2-}$ with ν_p 280 cm^{-1}, a molarity equilibrium constant may be calculated for the reaction of this complex to form $BiCl_6^{3-}$. To do so the following simplifying conditions are assumed: (1) all Bi(III) is in the form of $BiCl_6^{3-}$ when ν_p 263 cm^{-1} is reached; (2) essentially all Bi(III) is in the form of $BiCl_5^{2-}$ at ν_p 280 cm^{-1}; and (3) there is negligible contribution to the band height at 263 cm^{-1} from still lower species. From band heights of solutions with R = 8.0, 9.0, 13.0, and 16.0 the value so obtained for 43° is 1.3 ± 0.3 M^{-1}, in favorable agreement with the constant 0.7 M^{-1} determined in much more dilute solution at 20°.[4] It appears that $R_{max} = 5$ does indeed refer to $BiCl_5^{2-}$ with ν_p 280 cm^{-1}, ν_{dp} 235 cm^{-1} (from Figure 2), and bending modes near 115 cm^{-1}. Substantiating evidence is found in the spectrum of solid $(C_2H_5NH_3)_2$-$BiCl_5$, where the symmetric stretching frequency at 276 cm^{-1} compares well with ν_p 280 cm^{-1} in the $R = 6.0$ solution. The magnitude and direction of frequency deviation due to phase change are virtually identical with those for $BiCl_6^{3-}$.

The same may be said about the symmetric Bi–Cl stretching frequency in crystalline $C_6H_{13}N_2BiCl_4$ (290 cm^{-1}) compared to those solution frequencies (290 and 295 cm^{-1}) at which $R_{max} = 4.0$ in the Job analysis. Moreover, the reported conductivity of an acetone solution of this salt indicates that it contains discrete $BiCl_4^-$ units. Such a solution also has ν_p 290 cm^{-1}, a fact which strongly supports the claim for $BiCl_4^-$ species in aqueous solution. The stretching frequencies of the latter are probably near 293 and 256 cm^{-1}, while bending activity is seen near 115 cm^{-1}. These correspond to a solution of $R = 4.3$.

Because of their relatively low dielectric constant at the ambient lamp compartment temperature (43°), methanol (ϵ *ca.* 30) and 1-butanol (ϵ *ca.* 16) are expected to give solutions of $BiCl_3$ in which there is less self-ionization than in aqueous $HClO_4$. Hence, they should give spectra representative of purer solvated trichloro species. Bearing in mind the R values that these solutions contain (3.1 for methanol and 3.3 for 1-butanol) and the possible effect of solvent, the ν_p's obtained from these solutions at 305 and 302 cm^{-1} are in excellent agreement with the frequencies (305–310 cm^{-1}) at which $R_{max} = 3.0$ in Table I. In aqueous solution, therefore, it appears that $BiCl_3$(aq) can be assigned stretching frequencies near 307 and 272 cm^{-1} and bending activity near 120 cm^{-1}, corresponding to an $R = 3.3$ solution.

Several features in Figures 3 and 4 can now be interpreted. Each of the four solution species thus far identified possesses a finite intensity ratio of polarized band to depolarized band. The qualitative intensities of the solid spectra (Table II) show that in both $BiCl_4^-$ and $BiCl_5^{2-}$ the asymmetric stretch is of medium intensity relative to the strongest band. On the other hand, in the two $BiCl_6^{3-}$ salts the asymmetric stretch has relatively weak intensity. Since we are led to consider only the gross shape of the curve in Figure 4, because of experimental error and the position of the acetone solution point at $R = 4.0$, it is apparent that a similar situation exists in solution. Thus, $BiCl_4^-$ and $BiCl_5^{2-}$ exhibit roughly equal intensity ratios, whereas that of $BiCl_6^{3-}$ is considerably higher. The two data points from alcoholic $BiCl_3$ solutions lie below the general curve, since $BiCl_3$(solv) itself, undisturbed by $BiCl_4^-$, probably has a slightly lower ratio. Of course, solvent effects on the structure of the trichloro

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[27] L. I. Katzin and E. Gebert, *J. Am. Chem. Soc.*, **72**, 5455 (1950).

species may account for part of the difference. Later, the decrease in ratio at $R = 2.6$ will be correlated with other evidence to say something about the structure of complexes lower than $BiCl_3$(aq).

A sharpening of band width in complex systems like the present one suggests a trend toward fewer species. In Figure 3, the minima at $R = 3.0$ and 4.5 are easily explained in terms of $BiCl_3$(aq) and $BiCl_4^-$ gaining predominance in solutions with these respective formal ratios. Exactly why similar behavior is not observed for $BiCl_5^{2-}$ near $R = 6.0$ is uncertain. Perhaps it indicates a narrower range of existence for this complex, compared to the others. The broad maximum in $\omega_{1/2}$ centered near $R = 7.0$ probably arises from significant concentrations of all three species $BiCl_4^-$, $BiCl_5^{2-}$, and $BiCl_6^{3-}$ in these solutions.

Stepwise formation constants for the first and second chloro complexes of Bi(III) lie within the range 10^2–10^3.[28] Solutions with $R = 1.0$ and 2.0 should therefore contain predominantly $BiCl^{2+}$(aq) and $BiCl_2^+$(aq), respectively. Although the Raman bands are extremely weak and frequencies uncertain to ±5 cm^{-1} in these cases, the symmetric stretch of $BiCl^{2+}$(aq) and that of $BiCl_2^+$(aq) would both correspond to the band centered near 315 cm^{-1}. The intensity increase of the $R = 2.0$ spectrum relative to that of the $R = 1.0$ solution does not contradict the earlier proposal that two different species are present, since the change in mean molecular polarizability during vibration, and hence the Raman intensity, is expected to be greater when two Bi–Cl bonds per molecule are involved. Table III summarizes the Raman characteristics for the aqueous bismuth chloride species identified.

TABLE III
RAMAN SPECTRAL CHARACTERISTICS OF AQUEOUS $BiCl_n^{3-n}$ SPECIES

Species	Freq, cm^{-1} (polarization,[a] intensity[b])
$BiCl^{2+}$ (?)	*ca.* 315 (p, vw)
$BiCl_2^+$	*ca.* 315 (p, vw)
$BiCl_3$	307 (p, s), 272 (dp, m), *ca.* 120 (dp, m)
$BiCl_4^-$	293 (p, s), 256 (dp, m), *ca.* 115 (dp, w)
$BiCl_5^{2-}$	280 (p, s), 235 (dp, m), *ca.* 115 (dp, w)
$BiCl_6^{3-}$	263 (p, s), 220 (dp, w), *ca.* 110 (dp, w)

[a] p, polarized; dp, depolarized. [b] s, strong; m, medium; w, weak; v, very.

All evidence indicates that neither hydroxide nor chloride bridging exists in the aqueous bismuth chloride solutions studied here. Not only are the bands due to $Bi_6(OH)_{12}^{6+}$ absent, but the spectra are also virtually identical with those obtained in nonaqueous solvents, where hydroxide bridging is not feasible. The close similarity between solution spectra and the uncomplicated solid spectra points toward simple monomers in solution. Furthermore, the acetone solution of $C_6H_{13}N_2BiCl_4$, which presumably contains anionic $BiCl_4^-$(solv), gives a spectrum of exactly the same appearance as does an aqueous $R = 4.6$ solution.

The polarized line observed in dilute bismuth perchlorate solutions ($\lesssim 0.8\ M$) at *ca.* 390 cm^{-1} is undoubtedly due to the symmetric stretching motion of bismuth–water bonds, perhaps in the $Bi(H_2O)_x^{3+}$ ion. Furthermore, the polarized shoulder at 1040 cm^{-1} might be assignable to the BiO^+ stretching mode, in which case $BiO(H_2O)_x^+$ would be the relevant species. The gradual appearance of hexamer lines would then suggest that the predominant hydrolysis equilibrium is between $BiO(H_2O)_x^+$ and $Bi_6(OH)_{12}^{6+}$. This assignment for the 1040-cm^{-1} band is very uncertain. It is unlikely, though, that it arises from removal of degeneracy in the ClO_4^- ν_3 mode due to Bi(III)–ClO_4^- association. This would necessitate splitting of the ClO_4^- ν_4 band at 630 cm^{-1}, as well as general frequency shifts.[29] Neither is observed.

Bromide System.—The gradual fall in both frequency and half-width toward limiting values around $R = 8$ (ν 161, 137, and 57 cm^{-1}; $\omega_{1/2} = 37$ cm^{-1}) is clear evidence that the highest $BiBr_n^{3-n}$(aq) species has been formed almost completely at this formal ratio. Its stoichiometry is established primarily by the close similarity between these limiting solution frequencies and their relative intensities and the Bi–Br frequencies and intensities in solid $(N_2H_5)_3BiBr_6$. The frequencies differ by about 5 cm^{-1}, while the relative band intensities are roughly the same. In addition, the Job analysis of four sets of band heights (at 160, 150, 140, and 55 cm^{-1}) invariably associates $R_{\max} \sim 6$ with the highest species. Taken together, these results unequivocally point toward $BiBr_6^{3-}$ as the highest species in solutions studied here. The identity of the lower species indicated by the Job method has not been determined. Haight[5b] finds a formation constant of 0.1 M^{-2} for $BiBr_8^{5-}$. If this species is formed at all, it can be only in such low concentration as to be unobserved by the Raman technique, *i.e.*, with a formation constant less than 0.1 M^{-2}.

In the present Raman study, one of the most obvious differences between the chloride and bromide systems is in the R values at which spectral features reach limiting positions. Thus, ν_p and $\omega_{1/2}$ for the chlorides do not become constant until $R \sim 20$ ([Bi(III)] + [Cl$^-$] = 2.08), whereas for the bromides this occurs at $R \sim 8$ ([Bi(III)] + [Br$^-$] = 3.61). It may be concluded that $BiBr_6^{3-}$ forms much more readily in concentrated solution than does $BiCl_6^{3-}$. This has been found for more dilute solutions as well[4] and should not be surprising. It is a manifestation of the general electronic character of Bi(III) and is often related to more efficient orbital overlap between metal and larger bromide ligand. Most likely $BiBr_8^{5-}$ does not form, because destabilizing steric restrictions involved in eight-coordination favor the already quite stable $BiBr_6^{3-}$.

Structural Aspects.—It is reasonable to assign the three bands for both solid and solution hexahalobis-

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(28) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964, p 300.

(29) H. Brintzinger and R. E. Hester, *Inorg. Chem.*, **5**, 980 (1966).

muthates to the Raman-active A_{1g} (symmetric stretch), E_g (asymmetric stretch), and F_{2g} (bending) modes of a BiX_6^{3-} unit possessing O_h symmetry. This is supported by the finding of Atoji and Watanabe[18] that Bi(III) exhibits such octahedral coordination in $Co(NH_3)_6BiCl_6$, a compound completely isomorphous with $Co(NH_3)_6TlCl_6$, which contains octahedral $TlCl_6^{3-}$ anions.

Structural inferences concerning $BiCl_5^{2-}$ can be made from an X-ray investigation of "bismuth monochloride," as well as from X-ray studies on related chloroantimonate(III) solids. "Bismuth monochloride" contains $BiCl_5^{2-}$ in the form of what have been called distorted octahedra with chlorides at five corners.[17] While $SbCl_6^{3-}$ can exist as a regular octahedron in compounds like Rb_2SbCl_6,[30] $SbCl_5^{2-}$ is also found as a distorted octahedron in $(NH_4)_2SbCl_5$.[31] These results indicate that the $5s^2$ and $6s^2$ electrons can be stereochemically active in the five-coordinate species, whereas they are inactive in the six-coordinate anions. Although it cannot be proven with certainty from the Raman spectra, it is very likely that $BiCl_5^{2-}$ maintains this structure, owing to the $6s^2$ electrons, in solution as well.

The Raman spectrum of solid $C_6H_{13}N_2BiCl_4$ is sufficiently complicated so as not to allow straightforward interpretation. There are several possibilities for assignment. The pattern of observed bands (which need not comprise the complete spectrum) can be associated either with a molecule of originally D_{4h} or T_d symmetry which possesses a lower site symmetry in the crystal or with a molecule which is naturally distorted (to D_{2d}, for example) owing to the $6s^2$ electron pair or other effects. The stretching frequencies from the acetone solution (ν_p 290 cm^{-1}, ν_{dp} 255 cm^{-1}) are of little help in determining whether the solid structure, whatever it may be, is exactly maintained through the phase change, since solvent merging of spectral lines is not uncommon. The smooth trend in aqueous solution frequencies in going from $BiCl_4^-$ (ν_p 293 cm^{-1}) to $BiCl_5^{2-}$ (ν_p 280 cm^{-1}) and finally to $BiCl_6^{3-}$ (ν_p 263 cm^{-1}) suggests that the coordination geometry does not abruptly change from tetrahedral to octahedral. Such an abrupt transition has been found to occur in the aqueous thallium(III) chloride system with an accompanying large frequency decrease.[26,32] It appears, then, that $BiCl_4^-$ in solution is in some way distorted from T_d symmetry, perhaps by the effect of the stereochemically active $6s^2$ electron pair or through coordination of solvent.

The structure of solvated $BiCl_3$ is more definitely established from the Raman data. If the weak, broad depolarized band at *ca.* 120 cm^{-1} (when $R \sim 3$) actually consists of two lines, one polarized and the other depolarized, then all features of the complete four-line spectrum (*i.e.*, relative position and intensity) are typical of a pyramidal C_{3v} molecule. Such a species possesses four Raman-active vibrations: ν_1 (A_1, symmetric stretch), ν_2 (A_1, symmetric bend), ν_3 (E, asymmetric stretch), and ν_4 (E, asymmetric bend). As yet unpublished results from this laboratory indicate that the ν_2 (A_1) mode of a similar C_{3v} molecule, $AsCl_3$, is only weakly polarized. Consequently, the polarized nature of this line for $BiCl_3$(solv) on the Rayleigh shoulder could easily have been missed. The only likely alternative for the $BiCl_3$(solv) structure is planar D_{3h}. However, judging from molecules of known D_{3h} configuration, this symmetry requires a Raman-active asymmetric stretching mode at much too high a frequency to fit the data for $BiCl_3$(solv). We conclude that $BiCl_3$(solv) is pyramidal in both aqueous and alcoholic solution, probably with solvent coordination.

The species lower than $BiCl_3$ exhibit only one weak, symmetric polarized Raman band in our spectra. This is expected for the diatomic species $BiCl^{2+}$(aq). For $BiCl_2^+$(aq), it is unlikely that a weak depolarized asymmetric stretching band is hidden under the observed peak, because Job analysis data (Table I) never include $R_{max} < 3$ for band heights at any ν_{dp}. Moreover, the decrease through $R = 2.6$ in Figure 4 shows that a depolarized band probably does not exist in this area for $BiCl_2^+$(aq) but starts to appear only when $BiCl_3$(aq) is formed. A one-line spectrum for $BiCl_2^+$(aq) corresponds to a linear $D_{\infty h}$ species. It probably exists as such in solution, but the weakness of the spectrum does not permit a bent C_{2v} structure to be ruled out completely.

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[30] K. A. Jensen, *Z. Anorg. Allgem. Chem.*, **232**, 193 (1937).

[31] M. Edstrand, M. Inge, and N. Ingri, *Acta Chem. Scand.*, **9**, 122 (1955).

[32] T. G. Spiro, *Inorg. Chem.*, **4**, 1290 (1965).