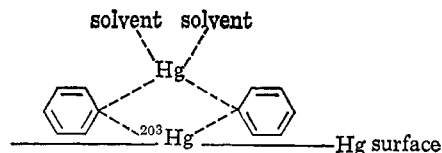


the adsorption process. Further experimental work with bulky groups in these positions is in progress. Though the reaction must be bimolecular with one reactant in excess, it is difficult to envisage any simple  $SE_2$  mechanism as this would involve the detachment of one of the rings, contrary to the results obtained with *p*-nitrophenylphenylmercury in part I. The only way to completely substitute the mercury atom is by two successive  $SE_2$  type processes during which any one ring is never completely detached, *i.e.*, a type of  $SE_i$  mechanism. As the products are essentially similar to the reactants, the potential energy diagrams should be symmetrical about the transition state. This must be postulated as



which is similar to that proposed by Reutov.<sup>3</sup> The use of the substituent constant  $(\sigma + \sigma^+)/2$  implies successive attack at each ring. However, the best Hammett plot was obtained using  $\sigma$  constants, so that it seems more likely that attack on both rings is virtually simultaneous, the van der Waals adsorption forces leading to chemical bonds in the transition state.

## The Vibrational Spectrum of the Hydrolytic Hexamer of Bismuth(III)<sup>1a</sup>

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**Abstract:** The Raman spectrum of hydrolyzed bismuth(III) perchlorate solutions and both Raman and infrared spectra of crystalline samples obtained from these solutions are reported. The clear agreement of solid and solution Raman spectra establish the similarity of the structural units in both phases. The spectral features are satisfactorily interpreted as arising from the normal vibrational modes of the octahedral cage complex,  $Bi_6(OH)_{12}^{6+}$ . There is no vibrational evidence for perchlorate binding either in solution or in the solid.

In recent years there has been a great deal of interest in the hydrolytic polymerization of metal ions. Along with the exhaustive potentiometric studies of Sillén and his co-workers,<sup>2</sup> which have established the near universality of polynuclear complex formation accompanying metal ion hydrolysis, there have been several investigations aimed at characterizing the polynuclear products by other methods. Ultracentrifugation,<sup>3</sup> light scattering,<sup>4</sup> and the coagulation method<sup>5</sup> have been applied to this task. Vibrational spectroscopy offers attractive possibilities in this direction, especially for the structural elucidation of hydrolytic polymers. To date these possibilities have been little explored, but a beginning has been made in the application of Raman spectroscopy.<sup>6,7</sup>

The hydrolysis of bismuth(III) has been particularly well characterized. Olin's potentiometric study,<sup>8</sup> the ultracentrifuge measurements of Holmberg, Kraus, and

Johnson,<sup>3</sup> and the light scattering results of Tobias and Tyree<sup>4</sup> are all in agreement that a single hydrolysis product,  $Bi_6(OH)_{12}^{6+}$ , predominates over a wide range of bismuth and hydrogen ion concentrations in perchlorate solution. Danforth, Levy, and Agron,<sup>9</sup> using solution X-ray scattering, established the structure of this complex as an octahedral array of bismuth ions bridged by hydroxyl groups, which are most probably located at each edge of the octahedron, although the bismuth-oxygen interactions could not be determined with precision. The high concentrations of hydrolyzed bismuth attainable in perchlorate solution and the high atomic weight of bismuth should ensure favorable intensities for Raman scattering, assuming some covalency for the bismuth-oxygen bonds. Consequently, we decided to begin a program of vibrational spectroscopic studies of metal ion hydrolysis with this system.

### Experimental Section

Two solutions of bismuth(III) were prepared by dissolving reagent grade  $Bi_2O_3$  (Baker and Adamson) in concentrated perchloric acid with overnight digestion to complete dissolution. Solution I was 4.87 *M* in bismuth and 6.85 *M* in perchlorate; solution II was 8.41 *M* in bismuth and 8.85 *M* in perchlorate. Solid samples for both Raman and infrared measurements were obtained by slow crystallization from solutions I and II. The crystals were ground to a fine powder in an agate mortar. The powder was pressed to remove excess perchloric acid, dried in an oven at

(1) (a) This investigation was supported in part by the National Science Foundation under Grant GP-3404 and in part by the Public Health Service under Grant GM-13498-01 from the National Institute of General Medical Sciences; (b) NASA Predoctoral Fellow.

(2) See L. G. Sillén, *Quart. Rev.* (London), **13**, 146 (1959), for an early review. An example of recent work is G. Biedermann and L. Newman, *Arkiv Kemi*, **22**, 203 (1964).

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(8) A. Olin, *Acta Chem. Scand.*, **13**, 1791 (1959).

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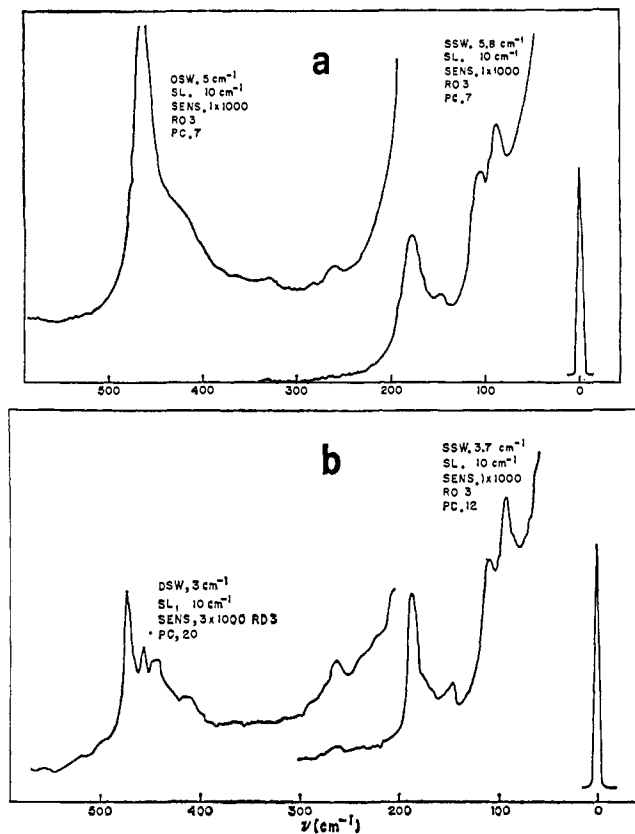


Figure 1. (a) Raman spectrum of solution I, (b) Raman spectrum of crystalline  $\text{Bi}_6(\text{OH})_{12}(\text{ClO}_4)_6$ : Cary Model 81; lamp current 15 amp; scan speed  $0.25 \text{ cm}^{-1}/\text{sec}$ . Abbreviations: SSW = single slit width; DSW = double slit width; SL = slit length; PC = period control; SENS = sensitivity setting; RD = Raman dynode setting.

$100^\circ$  overnight, and stored in a desiccator over "Drierite" prior to the taking of spectral measurements.

The solutions were analyzed for bismuth by precipitation as the phosphate, and for perchlorate by passage through a cation-exchange resin followed by titration with standard sodium hydroxide.

The Raman spectra were recorded at  $28 \pm 1^\circ$  on a Cary Model 81 Raman spectrophotometer using the 4358-A mercury line for excitation. A standard Cary 7-mm cell was used to obtain the solution spectra, and a conical cell constructed on the design of Busey and Keller<sup>10</sup> was used for the solid spectra. Polarization measurements on the liquid samples were made with polaroid cylinders surrounding the sample tube.

Infrared spectra in the region  $170\text{--}700 \text{ cm}^{-1}$  were taken with a Beckman IR-12 infrared spectrophotometer. The  $100\text{--}170\text{-cm}^{-1}$  region was measured with a Perkin-Elmer 301 infrared spectrophotometer. (This instrument was made available through the courtesy of RCA Laboratories, Princeton, N. J.) The samples were milled in Nujol and pressed between polyethylene windows.

## Results

**(A) Solution Spectra.** The Raman spectrum of solution I is shown in Figure 1a. Six distinct bands are observed in the region  $60\text{--}400 \text{ cm}^{-1}$ , and there is a shoulder at about  $447 \text{ cm}^{-1}$  on the  $462\text{-cm}^{-1}$  perchlorate band. The band at  $177 \text{ cm}^{-1}$  is polarized, and considerable polarization is observed for the  $447\text{-cm}^{-1}$  shoulder, which is shifted to about  $435 \text{ cm}^{-1}$  when the exciting light is polarized parallel to the direction of observation. The integrated intensity ratio of the  $462\text{-cm}^{-1}$  perchlorate band, with its  $447\text{-cm}^{-1}$  shoulder,

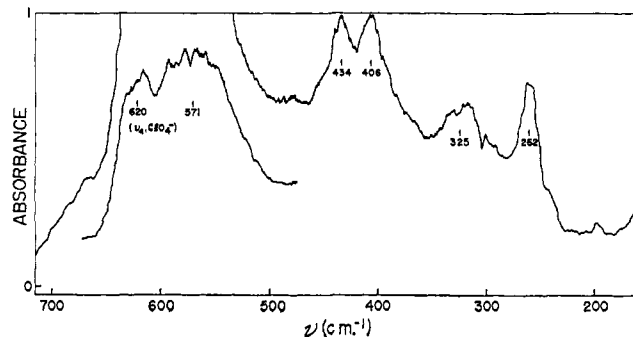


Figure 2. Infrared spectrum of crystalline  $\text{Bi}_6(\text{OH})_{12}(\text{ClO}_4)_6$  in Nujol mull: Beckman IR-12; double beam; gain, 6%; slit program, standard; period control, 8.

to the  $620\text{-cm}^{-1}$  perchlorate band is 2.13 in nonpolarized light, but decreases to 1.46 in parallel polarized light. For sodium perchlorate solutions the intensity ratio of the two perchlorate bands is 1.09. This behavior suggests that the  $447\text{-cm}^{-1}$  shoulder is a composite of bands at least one of which is totally symmetric.

Solutions I and II were prepared to contain widely different bismuth and hydrogen ion concentrations in order to investigate the possibility that the observed bands are due to different species. If it is assumed that the predominant species is  $\text{Bi}_6(\text{OH})_{12}^{+6}$ , the concentration of hydrogen ion is  $2.0 \text{ M}$  in solution I and  $0.4 \text{ M}$  in solution II. The spectra of the two solutions were identical.

**(B) Solid Spectra.** The solid samples obtained from either solution I or solution II gave the Raman spectrum in Figure 1b. The spectrum of the solid in the region  $60\text{--}270\text{-cm}^{-1}$  shows the same features as that of the solution (with slight frequency shifts) except for background peaks at  $145$  and  $170 \text{ cm}^{-1}$  which appear in all solid spectra.<sup>11</sup> The band at  $340 \text{ cm}^{-1}$  in solution is absent in the solid spectrum, and the shoulder at  $447 \text{ cm}^{-1}$  in solution is resolved into three frequencies in the solid spectrum, at  $407$ ,  $440$ , and  $451 \text{ cm}^{-1}$ .

The infrared spectrum of the solid (Figure 2) shows six bands in the region  $170\text{--}700 \text{ cm}^{-1}$ . The band at  $620 \text{ cm}^{-1}$  is attributed to the  $\nu_4$  (infrared active) perchlorate frequency. The spectrum below  $170 \text{ cm}^{-1}$  was essentially featureless except for a broad absorption in the region  $100\text{--}160 \text{ cm}^{-1}$ .

## Discussion

Both solution and solid Raman spectra show the four bands characteristic of free perchlorate.<sup>12</sup> The absence in the infrared spectrum of the  $\nu_2$  ( $460 \text{ cm}^{-1}$ ) perchlorate band (infrared inactive when perchlorate is free, active when bound) serves as a further confirmation that the perchlorate is not bound firmly to the bismuth species.

The vibrational frequencies attributable to bismuth species are tabulated in Table I. The close correspondence of solution and solid Raman spectra clearly establishes the structural identity of the species in both phases. Since Danforth, *et al.*,<sup>9</sup> showed that the predominant solution species is octahedral  $\text{Bi}_6(\text{OH})_{12}^{+6}$ , we can conclude, in the absence of crystal structure

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Table I. Vibrational Frequencies (cm<sup>-1</sup>) Attributable to Bismuth Species<sup>a</sup>

| Raman                 |  | Solid | Infrared Solid |
|-----------------------|--|-------|----------------|
| Solution              |  |       |                |
| 88 dp                 |  | 90    | ?              |
| 107 dp                |  | 108   | ?              |
| 148 dp                |  | ~147  | ?              |
| 177 p                 |  | 187   | ...            |
| 258 dp                |  | 263   | 263            |
| ...                   |  | ...   | 325            |
| 340 ?                 |  | ...   | ...            |
| (407) <sup>b</sup> dp |  | 407   | 406            |
| (435) <sup>b</sup> dp |  | 440   | 434            |
| ~447 p                |  | 451   | ...            |
| ...                   |  | ...   | 571            |

<sup>a</sup> Symbols: p, polarized; dp, depolarized; ..., absent; ?, uncertain. <sup>b</sup> Not resolved but believed to be present.

data, that the solid contains the same units, and should be formulated as Bi<sub>6</sub>(OH)<sub>12</sub>(ClO<sub>4</sub>)<sub>6</sub>.

For octahedral Bi<sub>6</sub>(OH)<sub>12</sub><sup>6+</sup>, the representation of the normal coordinates is (neglecting the hydrogen atoms)

$$\Gamma_{\text{total}} = 2A_{1g} + A_{2g} + 3E_g + 3T_{2g} + A_{2u} + E_u + 5T_{1u} + 3T_{2u} + 3T_{1g}$$

Subtracting the representations corresponding to translations, rotations, and vibrations inactive in either the Raman or infrared leaves  $\Gamma_{\text{vib}} = 2A_{1g} + 3E_g + 3T_{2g} + 4T_{1u}$  or eight Raman-active and four infrared-active fundamentals with no coincidence of the Raman and infrared bands due to the presence of a center of symmetry.

The broad shoulder at 447 cm<sup>-1</sup> in solution probably contains the bands observed in the solid at 407, 440, and 451 cm<sup>-1</sup>. From the shift in the shoulder to lower frequencies in parallel polarized light, we conclude that the 451-cm<sup>-1</sup> band in the solid corresponds to one of the two predicted A<sub>1g</sub> fundamentals, the other one giving rise to the polarized band at 177 cm<sup>-1</sup> (187 cm<sup>-1</sup> in the solid). There remain, then, seven ob-

served Raman bands where six are expected. However, the weak 340-cm<sup>-1</sup> solution band is not present in the solid spectrum. It seems likely that it does not correspond to a Bi<sub>6</sub>(OH)<sub>12</sub><sup>6+</sup> fundamental but arises, perhaps, from an interaction of solvent water with the bismuth species.

Three of the five observed infrared bands appear to be coincident with Raman bands and therefore violate the exclusion principle. Most likely this violation is the result of distortion in crystalline Bi<sub>6</sub>(OH)<sub>12</sub>(ClO<sub>4</sub>)<sub>6</sub> which results in loss of the center of inversion. It is physically reasonable that the bismuth cage may undergo a slight trigonal distortion on crystallization leading to D<sub>3</sub> site symmetry. This point group accounts well for the observed coincidences as well as for the absence of the A<sub>1</sub> bands in the infrared spectrum, these being infrared inactive in D<sub>3</sub>. The two noncoincident infrared bands presumably arise from two of the expected T<sub>1u</sub> fundamentals of the octahedral cage.

The eight Raman-active fundamentals attributed to the cage are divided into two well-separated regions: 80–200 cm<sup>-1</sup> and 400–500 cm<sup>-1</sup>, with the 263-cm<sup>-1</sup> band occupying an intermediate position. It seems likely that the low-frequency bands involve primarily bending modes and those above 400 cm<sup>-1</sup> primarily stretching modes of the Bi–O bonds. Presumably the A<sub>1g</sub> fundamental at 447 cm<sup>-1</sup> (451 cm<sup>-1</sup> in the solid) is the “breathing” mode of the octahedral cage, while the one at 177 cm<sup>-1</sup> (187 cm<sup>-1</sup> in the solid) is the symmetric mode in which the bismuth and oxygen atoms vibrate out of phase with one another. Such a motion would involve almost entirely bond bending. The two observed infrared bands which presumably arise from T<sub>1u</sub> fundamentals of the cage are in the primarily stretching region. The two remaining T<sub>1u</sub> modes are probably at frequencies lower than 170 cm<sup>-1</sup>. They may be masked by many other absorptions resulting from site symmetry-allowed vibrations, crystal lattice vibrations, etc., which no doubt produce the generally featureless infrared absorption observed in this region.