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Low-Frequency Vibrational Spectra of Bromo- and Iodobismuthates and the Observation of a Trans Effect

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The far-infrared and Raman spectra of 17 bismuth halide complexes of formulas $\mathrm{BiX_6^{3-}}$, $\mathrm{BiX_5^{2-}}$, $\mathrm{Bi_2X_9^{3-}}$, and $\mathrm{BiX_4^-}$ have been recorded for X = Br or I. The spectra of these anions, which show bands only below 200 cm^{-1}, have been analyzed in terms of known structures. Several of the spectra have been used to confirm predicted structures for other molecules. Although the solid-state spectra are seen to vary somewhat with the cation present, they can be used to distinguish between the different types of complexes. These spectra also establish frequency ranges expected for Bi–Br and Bi–I stretches, for both the external and the bridging types. Approximate force constants were calculated for the various types of Bi–X stretches; from these it was determined that the nature of the bonding of the halide trans to a particular Bi–X bond significantly affects the strength of that bismuth–halogen bond. Moreover, the strength of the Bi–X bonds was found to be greatest in the anions in which the largest number of the other bonds were to bridged halogens.

Introduction

The compounds of the type $\mathrm{R_\mathit{l}Bi_\mathit{m}X_\mathit{n}}$ where R represents an amine cation and X = Br or I have been known for over a hundred years.[1-3] A variety of compounds with n/m ratios ranging from 4 to 6 have more recently been prepared by Whealy and co-workers.[4,5] It was demonstrated that the principal factor determining the composition of the complex was the nature of the cation. The crystal structures of some of these complexes including $\mathrm{BiBr_4^-}$, $\mathrm{BiI_4^-}$, $\mathrm{BiBr_5^{2-}}$, and $\mathrm{BiBr_6^{3-}}$ have been determined by X-ray analysis.[6-8] Suprisingly, even bond lengths expected to be equivalent were found to have different values for these ions. The same was true for bond angles.

Because of the complex nature of these molecules, it was apparent that vibrational data would be valuable in helping to understand them better. Moreover, it was desirable to see whether the structures of the various molecules could be determined from their far-infrared and Raman spectra. Consequently, the vibrational spectra of a large number of complexes containing the following anions were analyzed: $\mathrm{BiBr_6^{3-}}$, $\mathrm{BiBr_5^{2-}}$, $\mathrm{BiBr_4^-}$, $\mathrm{Bi_2Br_9^{3-}}$, $\mathrm{BiI_6^{3-}}$, $\mathrm{BiI_4^-}$, $\mathrm{Bi_2I_9^{3-}}$.

Previous infrared and Raman studies have dealt with the possibility of a stereochemically active lone pair on bismuth and with the structural differences between the solution and crystalline forms of $\mathrm{BiX_4^-}$ and $\mathrm{BiX_5^{2-}}$. Ahlijah and Goldstein[9,10] state that these complexes are distorted tetrahedra with C_{2v} symmetry both in solution and in crystalline form. However, other vibrational work[11,12] supports the conclusions from X-ray studies[6,7,13] that the complexes are chain polymeric as solids.

Experimental Section

Samples of the bromo- and iodobismuthates were prepared as described by Whealy and co-workers[4,5] and stored in a vacuum desiccator. Far-infrared spectra of the solids were run by using a Perkin-Elmer FIS-3 spectrophotometer. Nujol mulls, prepared from mineral oil dried over fresh sodium metal, of the samples were smeared onto thin polyethylene plates. Laser Raman spectra of the solids were recorded directly by using a Cary 82 spectrometer and a Coherent Radiation 52K krypton laser. The 6471-Å exciting line operated at 100 mW was generally used except for several samples which decomposed under these conditions. The 6731-Å line was used for those compounds. Raman spectra of aqueous $\mathrm{BiBr_6^{3-}}$ and $\mathrm{BiI_6^{3-}}$ solutions were obtained by using 0.01 M concentrations of the anion and at least a 12-fold excess of the $\mathrm{Br^-}$ or $\mathrm{I^-}$ ion. The solutions were contained in standard capillary tubes.

Results and Discussion

Figure 1 shows the simplified structures for the four types of bismuthates studied. The structure of $\mathrm{Bi_2X_9^{3-}}$ is assumed but is supported by this work. In each structure the bismuth atom is surrounded by a distorted octahedron of halogen atoms. Even in the $\mathrm{BiX_6^{3-}}$ complexes, several different bond lengths and bond angles are present. The $\mathrm{BiX_5^{2-}}$ and the $\mathrm{BiX_4^-}$ structure are part of polymeric systems in which the units are linked by bridging halogen atoms. For analyzing the spectra the symmetries of the latter two complexes are both taken to be C_{2v}; $\mathrm{Bi_2X_9^{3-}}$ was assumed to be D_{3h} and $\mathrm{BiX_6^{3-}}$ to be O_h. It is known from the X-ray studies, however, that these structures are in actuality distorted.[6-8] Table I summarizes the symmetry species for the vibrations of these complexes on the basis of the assumed symmetry point groups.

Figures 2 and 3 show the far-infrared and Raman spectra characteristic of the different complexes. The former is for the bromobismuthates and the latter for iodo compounds. The far-infrared bands are generally very broad, and the accuracy of the band centers is typically ±5 cm^{-1}. The Raman peaks on the other hand are generally sharper (±2 cm^{-1}), and these have been used for the vibrational assignments where possible. The individual spectra will now be discussed.

$\mathrm{BiBr_6^{3-}}$ Complexes. Table II lists the far-infrared and Raman frequencies for four different $\mathrm{R_3BiBr_6}$ compounds as well as the Raman spectrum of aqueous $\mathrm{BiBr_6^{3-}}$. The only infrared-active Bi–Br stretching mode, ν_3 ($\mathrm{T_{1u}}$), for an undistorted octahedral structure is observed as a very intense band in the 123–130-cm^{-1} region for these complexes. Due to the distortions in the structure, three of these complexes also have infrared bands in the 150–158-cm^{-1} region corresponding to ν_1 ($\mathrm{A_{1g}}$) even though $\mathrm{A_{1g}}$ modes should be infrared inactive. This same symmetric stretching mode gives rise to the strongest Raman line at a similar frequency. In aqueous solution the Raman frequency is 161 cm^{-1}, and the line is polarized. The ν_2 ($\mathrm{E_g}$) stretching mode shows up as a weaker Raman line in all four compounds in the 129–142-cm^{-1} region and at 133 cm^{-1} in aqueous solution.

Of the bending modes only ν_4 ($\mathrm{T_{1u}}$) is infrared active and probably is associated with bands centered near 110 cm^{-1}. The ν_5 ($\mathrm{T_{2g}}$) mode is Raman active and shows up in aqueous solution at 63 cm^{-1} and in the four solid samples in the 63–65-cm^{-1} range. The other bending mode, ν_6 ($\mathrm{T_{2u}}$), should be

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Table I. Symmetry Species for the Vibrations of Halobismuthates

	molecule			
	BiX_6^{3-}	BiX_5^{2-}	BiX_4^{-}	$Bi_2X_9^{3-}$
assumed symmetry	O_h	C_{2v}	C_{2v}	D_{3h}
IR activity	T_{1u}	A_1, B_1, B_2	A_1, B_1, B_2	E', A_2''
Raman activity	A_{1g}, E_g, T_{2g}	A_1, A_2, B_1, B_2	A_1, A_2, B_1, B_2	A_1', E', E''
BiX stretches (external)	$A_{1g} + E_g + T_{1u}$	$2 A_1 + B_1 + B_2$	$A_1 + B_1$	$A_1' + E' + A_2'' + E''$
BiX stretches (bridging)		$A_1 + B_1$	$2 A_1 + B_1 + B_2$	$A_1' + E' + A_2'' + E''$
bending	$T_{1u} + T_{2g} + T_{2u}$	$3 A_1 + 2 A_2 + 2 B_1 + 2 B_2$	$3 A_1 + 2 A_2 + 2 B_1 + 2 B_2$	$2 A_1' + A_2' + 3 E' + A_1'' + A_2'' + 2 E''$

Table II. Vibrational Frequencies (cm^{-1}) of $BiBr_6^{3-}$ Complexes[a]

	CH_3NH_3[c]		$C_6H_5CH_2NH_3$[c]		n-$C_3H_7NH_3$[c]		$C_3H_5NH_3$[c]		
Raman[b]	IR	Raman	IR	Raman	IR	Raman	IR	Raman	assignt
161 s, P	152 sh	154 (10)	158 s	157 (10)		157 (10)	150 sh	158 (10)	ν_1 (A_{1g})
133 w, D		~135 (1) sh		129 (1)		138 (3)		142 (2)	ν_2 (E_g)
	126 s, br		124 vs		123 vs		130 s		ν_3 (T_{1u})
			111 sh		(70–180 vbr)		102 sh		ν_4 (T_{1u})?
				98 w		93 (2)		95 (2)	?
				84 (2)					?
63 m, ?		63 (17)		65 (2)		63 (7)		64 (7)	ν_5 (T_{2g})
				57 (2)					ν_6 (T_{2u})?
		27 (2)		34 (2)					lattice modes
		15 (8)		22 (5)		22 (3)			
				10 (2)					

[a] Relative Raman intensities given in parentheses. s = strong, m = medium, w = weak, sh = shoulder, br = broad, v = very, P = polarized, D = depolarized. [b] H_2O solution. [c] Cation.

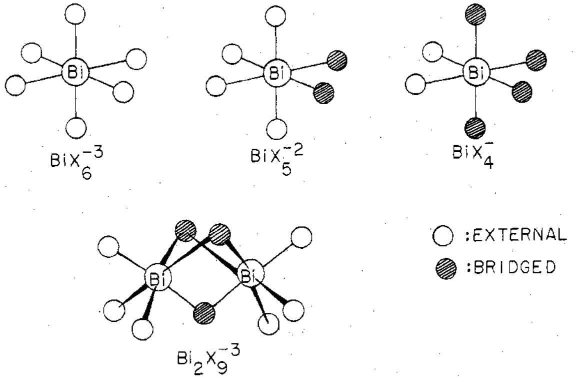

Figure 1. Structures of halobismuthates.

totally inactive but may be observed at 57 cm^{-1} for $(C_6H_5CH_2NH_3)_3BiBr_6$ in the Raman spectrum. Several lattice modes are observed in the Raman spectra as bands between 15 and 34 cm^{-1}.

$BiBr_5^{2-}$ Complexes. The vibrational frequencies of the polymeric R_2BiBr_5 complexes are listed in Table III, and the spectra for R = 4-picolinium are shown in Figure 2. For a C_{2v} model the A_1 external (cis) stretching vibration is seen to give rise to the strongest Raman line, at 169 cm^{-1} for the 4-picolinium complex and at 180 cm^{-1} for the pyridinium compound. The strong infrared bands at 159 and 157 cm^{-1} for the 4-picolinium and pyridinium complexes arise from the B_2 antisymmetric (trans) stretching. Raman lines at 156 and 166 cm^{-1} most likely correspond to the A_1 external stretching mode. The 142-cm^{-1} band for the 4-picolinium complex probably arises from the B_1 external (trans) antisymmetric stretching. The B_1 bridging antisymmetric stretch at 122 cm^{-1} for the 4-picolinium compound and at 108 cm^{-1} for the pyridinium compound shows considerable frequency dependence on its cation. The A_1 bridging symmetric stretch is seen as a broad Raman band at 114 cm^{-1} for the 4-picolinium compound. The nine bending vibrations give rise to bands in the 60–90-cm^{-1} region. Raman lines near 78, 72, and 60 cm^{-1} probably came from the A_1 modes whereas the broad infrared band near 80 cm^{-1} arises from its antisymmetric modes. The lattice modes can be observed in the Raman spectra between 22 and 51 cm^{-1}.

Table III. Vibrational Frequencies (cm^{-1}) of $BiBr_5^{2-}$ Complexes

4-picolinium[a]		pyridinium[a]		
IR	Raman	IR	Raman	assignt
	169 (10)		180 (10)	Bi–Br (external) str
159 ms	156 (5)	157 s	166 (1)	
	142 (1)			
122 s, br	131 w	108 vs		Bi–Br (bridge) str
	114 (2) bd			
83 ms, br	78 (4)	~80 sh	90 sh	bending modes
	68 (4)		75 (3)	
	60 (3)			
	51 (1)		46 (1)	lattice modes
	47 w, 41 w			
	32 (3), 25 (5)		32 (2), 22 (3)	

[a] Cation.

Table IV. Vibrational Frequencies (cm^{-1}) of $Bi_2Br_9^{3-}$ Complexes

Et_3NH[a]		i-Bu_2NH_2[a]		
IR	Raman	IR	Raman	assignt
	182 (10)		180 (10)	Bi–Br (external) str
163 vs	163 w, sh	161 vs	165 (3)	
	158 (3)			
	145 (1)			
	123 (1)		122 w	Bi–Br (bridge) str
99 vs		103 vs		
	69 (7)		70 (4) br	bending mode
	47 (4)		44 (1)	lattice modes
	26 (2), 15 (1)		35 (1), 22 (2)	

[a] Cation.

$Bi_2Br_9^{3-}$ Complexes. Figure 2 shows the far-infrared and Raman spectra of the triethylamine complex of $Bi_2Br_9^{3-}$, and Table IV lists the frequencies for this as well as the diiso-

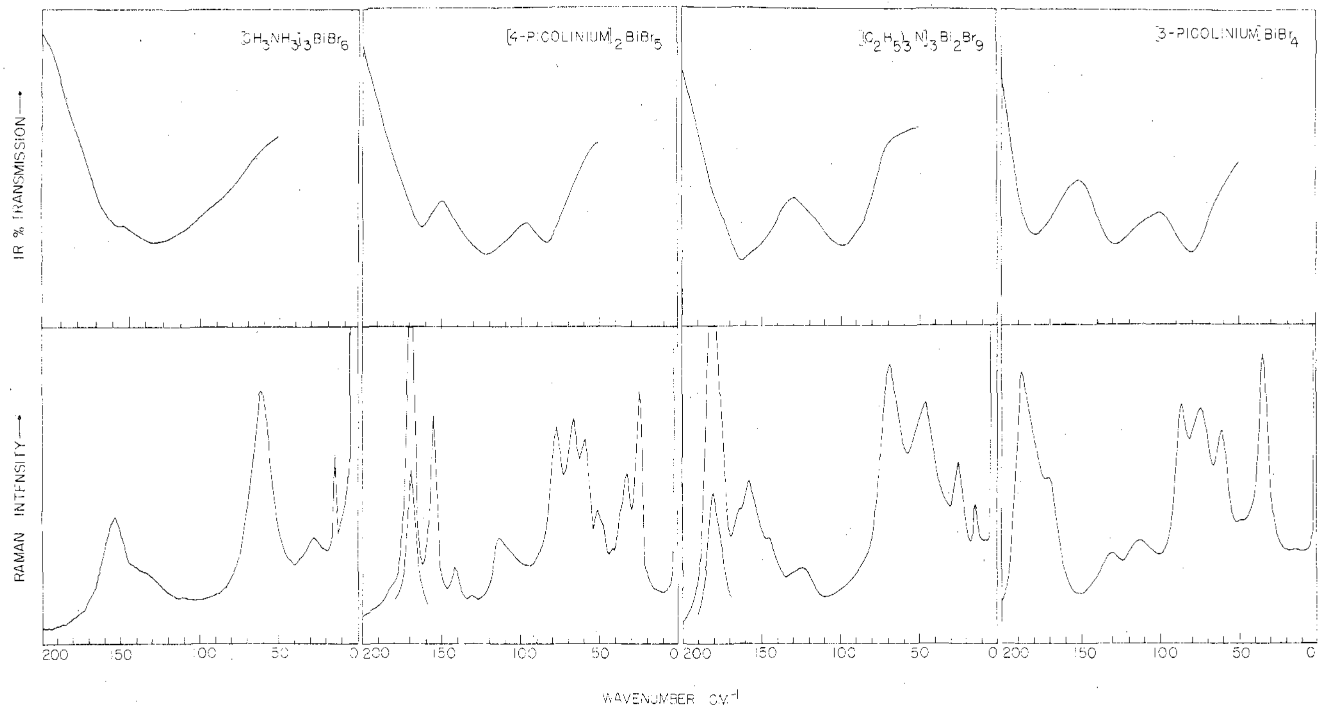

Figure 2. Far-infrared and Raman spectra of bromobismuthates.

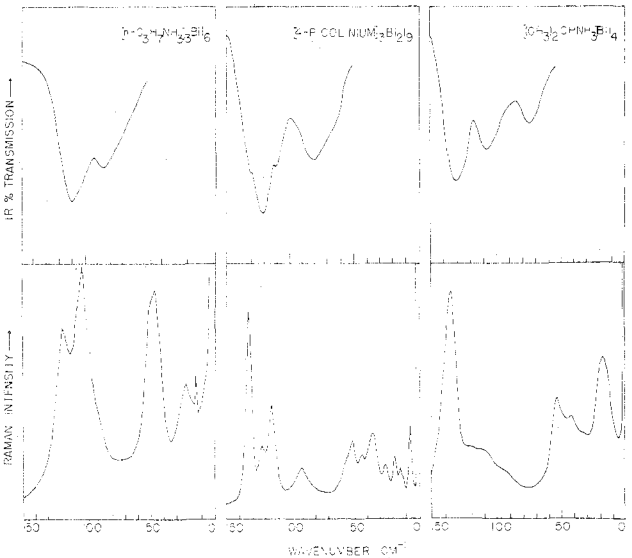

Figure 3. Far-infrared and Raman spectra of iodobismuthates.

butylammonium complex. The intense Raman lines at 182 and 180 cm^{-1} for the two complexes clearly correspond to the A_1' symmetric $BiBr_3$ stretching mode of the external bromines while the broad, very intense infrared bands with corresponding weak Raman lines near 163 cm^{-1} are due primarily to the antisymmetric E′ stretching mode. The stretching frequencies for the bridged Bi–Br–Bi stretches give rise to a very intense, broad infrared absorption near 100 cm^{-1} (E′) and weak Raman lines near 122 cm^{-1} (A_1'). The symmetric bending (A_1') of the external $BiBr_3$ groups gives rise to a strong Raman line near 70 cm^{-1} while the symmetric bending of the bridging groups may account for bands near 47 cm^{-1}. Two lattice modes for each complex were also observed.

$BiBr_4^-$ Complexes. The infrared and Raman spectra of the 3-picolinium $BiBr_4^-$ complex are shown in Figure 2, and the frequency tabulation for this and the quinolinium complex can be seen in Table V. The most intense Raman bands at 186 and 188 cm^{-1} in each spectrum result from the A_1 $BiBr_2$ symmetric stretch (external) while the antisymmetric stretching of this group gives rise to the strong infrared bands at 179 cm^{-1}. The corresponding moderately intense Raman lines appear as shoulders near 173 cm^{-1}. The four stretches of the bridged bromides have their frequencies bunched in the 110–134-cm^{-1} range with the two A_1 modes occurring near 134 and 120 cm^{-1} for the quinolinium complex and with the B_1 and B_2 modes at 131 and 110 cm^{-1}. Of the nine bending modes three are totally symmetric and give rise to bands at

Table V. Vibrational Frequencies (cm^{-1}) of $BiBr_4^-$ Complexes

quinolinium[a]		3-picolinium[a]		
IR	Raman	IR	Raman	assignt
	186 (10)		188 (10)	Bi–Br (external) str
179 s	173 (3)	179 s	173 (3)	
131 s	134 (3)	130 s	132 (1)	Bi–Br (bridge) str
	120 (1)		114 (2)	
110 m, sh				
	87 sh		87 (6)	bending modes
82 s	80 (9)	80 s		
			75 (6)	
	67 (10)		62 (5)	
	60 sh			
	47 (3)			lattice modes
	36 (10)		35 (8)	
	27 (1)			

[a] Cation.

Table VI. Vibrational Frequencies (cm^{-1}) of BiI_6^{3-} Complexes

	n-$C_3H_7NH_3$[b]		$Cr(en)_3$[b]		
Raman[a]	IR	Raman	IR	Raman	assignt
130 s, P		119 (7)		139 (10)	ν_1 (A_{1g})
	110 s		135 s		ν_3 (T_{1u})
110 w, D		105 (10)		128 (5)	ν_2 (Eg)
	84 ms	~90 vw	86 ms	84 w	ν_4 (T_{1u})?
55 w, ?		59 (2)			ν_5 (T_{2g})
		49 (4)		47 (8)	ν_6 (T_{2u})?
		34 (1), 23 w		22 (3)	lattice modes
		14 (3)		14 (2)	

[a] H_2O solution. [b] Cation.

Table VII. Vibrational Frequencies (cm^{-1}) of $Bi_2I_9^{3-}$ Complexes

$(CH_3)_2NH_2$[a]		piperidinium[a]		4-picolinium[a]		
IR	Raman	IR	Raman	IR	Raman	assignt
	138 (10)		135 (10)	~134 sh	134 (10)	Bi–I (external) str
128 s		129 s	124 w	123 s	123 (1)	
~110 sh	112 (3)	~114 sh	112 (2)	113 sh	116 (4)	
	99 (2)		99 (2)		92 (1)	Bi–I (bridge) str
83 m		85 m		80 ms		
	55 (3)		55 (5)		57 w	bending modes
			50 sh		53 (3)	
	40 (6)				45 w	
			37 (2)		37 (3)	lattice modes
			33 (2)			
	19 w		22 (1)		25 (1), 18 (1)	
			13 (1)		14 w, 7 (3)	

[a] Cation.

Table VIII. Vibrational Frequencies (cm^{-1}) of BiI_4^- Complexes

n-$C_3H_7NH_3$[a]		$(CH_3)_2CHNH_3$[a]		
IR	Raman	IR	Raman	assignt
139 s	143 (10)		139 (10)	Bi–I (external) str
130 s	134 (9)	131 (s)		
118 m	113 (1)	107 ms	~113 w	Bi–I (bridge) str
	97 (1)		95 w	
79 s	82 w	73 m		bending modes
	59 w		55 (5)	
	52 (4)		44 (2)	
	29 (5)			lattice modes
	19 (5), 13 (4)		20 (4)	

[a] Cation.

Table IX. Bi–X Stretching Frequencies (cm^{-1})

X	type	BiX_6^{3-}	BiX_5^{2-}	BiX_4^-	$Bi_2X_9^{3-}$
Br	external	123–158	142–180	173–189	145–180
	bridge		108–131	110–134	99–123
I	external	105–139		130–143	110–138
	bridge			95–118	80–99

Table X. Raman Frequencies[a] (cm^{-1}) and UBFF Force Constants (mdyn/A) for Octahedral BiX_6^{3-} Molecules

X	ν_1	ν_2	ν_5	K	H	F	F'
Cl	260	215	100	0.88	−0.03	0.14	−0.01
Br	161	133	63	0.79	0.00	0.09	−0.01
I	130	110	55	0.96	0.00	0.11	−0.01

[a] Frequencies for $BiCl_6^{3-}$ from ref 19.

87, 75, and 62 cm^{-1} in the Raman spectrum of the 3-picolinium complex. Several lattice modes were observed below 50 cm^{-1}.

BiI_6^{3-} Complexes. Figure 3 shows the infrared and Raman spectra of the propylammonium BiI_6^{3-} complex while Table VI lists the frequencies for both the n-$C_3H_7NH_3^+$ and $Cr(en)_3^{3+}$ complexes. The observed frequencies are substantially different from each other and from the aqueous solution spectra. The totally symmetric stretch ν_1 occurs at 119, 139, and 130 cm^{-1} while ν_2 is at 105, 128, and 110 cm^{-1} for the n-$C_3H_7NH_3^+$, $Cr(en)_3^{3+}$, and aqueous systems, respectively. Two infrared bands were observed for each solid complex, and these are due to ν_3 (at 110 or 135 cm^{-1}) and ν_4 (at 84 cm^{-1}). Other assignments are also listed in the table.

$Bi_2I_9^{3-}$ Complexes. The vibrational spectra of $R_3Bi_2I_9$ complexes for R = $(CH_3)_2NH_2^+$, piperidinium, and 4-picolinium are listed in Table VII, and the spectra are shown for the latter in Figure 3. The A_1' symmetric BiI_3 stretching mode shows strong Raman intensity near 135 cm^{-1} for all complexes while the E′ and E″ bands can be observed in both infrared and Raman spectra near 124 and 112 cm^{-1}. The stretching of the bridged iodines give rise to Raman bands near 99 cm^{-1} due to the A_1' symmetric stretching mode and to infrared bands near 83 cm^{-1} due to the E′ (or A_2'') vibration. The bending modes occur between 40 and 55 cm^{-1}, and the lattice modes are lower still.

BiI_4^- Complexes. Figure 3 displays the spectra of $RBiI_4$ for R = $(CH_3)_2CHNH_3$, and Table VIII lists the frequency assignments for both this and the R = $C_3H_7NH_3$ complex. The spectra of both are similar except that the latter shows more coincidences between the infrared and the Raman spectra. The A_1 symmetric BiI_2 stretching (external) mode has a frequency near 140 cm^{-1} while the B_1 antisymmetric vibration occurs at about 130 cm^{-1}. Frequencies for the stretching of the bridged iodines occur near 113 and 95 cm^{-1} while bending modes range from 44 to 82 cm^{-1}. It is noteworthy that for the BiI_4^- complexes, as well as for the others with bridging Bi–X–Bi groups, the intensities of the infrared and Raman bands for stretches are considerably less for bridged groups than for the externally bound Bi–X groups.

Summary of Frequency Assignments. Table IX puts into perspective the frequency ranges for the seven different kinds of complexes. Overall the frequencies of external Bi–Br stretches can be seen to range from 123 to 189 cm^{-1} while the bridged groups have frequencies from 99 to 134 cm^{-1}. Corresponding Bi–I frequencies are, of course, lower with external Bi–I stretches in the 105–143-cm^{-1} range while the bridged Bi–I stretches occur between 80 and 118 cm^{-1}. The different types of $Bi_mX_n^{p-}$ complexes can also readily be distinguished from each other by use of the spectra. The BiX_4^- ions have the highest frequency ranges for both external and bridged Bi–X stretches, whereas the BiX_6^{3-} complexes have the lowest frequencies for the external stretches. The BiX_5^{2-} and $Bi_2X_9^{3-}$ frequencies are intermediate with those for the bridging Bi–X groups in the latter being the very lowest. It is also significant that the observed spectra correspond well to what would be predicted for the X-ray determined or assumed structures. The BiX_6^{3-} complexes show the expected Raman lines and the most intense infrared bands for O_h symmetry. In addition, other bands were also observed to result from the distortions to the high symmetry. For the other complexes both the external and bridging stretching modes were well-defined. In the Raman spectra the totally symmetric modes, especially for the external Bi–X bonds, produced the strongest lines while the antisymmetric stretches gave rise to the most intense infrared bands. The symmetric bending modes could generally be observed in Raman spectra, but the distinction between these and the lattice vibrations is not always obvious. A few antisymmetric bending modes were also evident in the far-infrared spectra.

Calculation of Force Constants. For most of these complexes a complete normal-coordinate analysis is not possible due to insufficient data for the bending modes and the lack of data

Table XI. Stretching Frequencies (cm^{-1}) and Force Constants (mdyn/Å) for Bi-X Bonds

bridging halogens	anion	type	trans halogen	ν_{sym}	$\nu_{antisym}$	f_R	f_{RR}[a]
0	$BiBr_6^{3-}$	external	external	161, 133	126	0.69	0.27^t, 0.07^c
2	$BiBr_5^{2-}$	external (cis)	bridging	175	158	0.95	0.10^c
		external (trans)	external	161	142	0.88	0.34^t
		bridging	external	~115		~0.45	
3	$Bi_2Br_9^{3-}$	external	bridging	181	162	0.97	0.07^c
		bridging	external	~111		~0.42	
4	$BiBr_4^-$	external	bridging	186	176	1.12	0.06^c
		bridging	external and bridging	~122		0.51	
0	BiI_6^{3-}	external	external	130, 105	110	0.70	0.29^t, 0.08^c
3	$Bi_2I_9^{3-}$	external	bridging	136	125	0.77	0.04^c
		bridging	external	~90		~0.38	
4	BiI_4^-	external	bridging	141	132	0.87	0.06^c
		bridging	external and bridging	~105		~0.52	

[a] t and c refer to stretch–stretch interaction constants between trans and cis groups, respectively. The octahedral constants were calculated from the stretching frequencies ν_1 (A_{1g}), ν_2 (E_g), and ν_3 (T_{1u}) by using the relations $F_{11}(A_g) = f_R + f_{RR}^t + 4f_{RR}^c$, $F_{22}(E_g) = f_R + f_{RR}^t - 2f_{RR}^c$, and $F_{33}(T_{1u}) = f_R - f_{RR}^t$ and similar **G** matrix relationships.

for isotopically substituted molecules. For the octahedral BiX_6^{3-} complexes there is in principle enough data to determine a Urey–Bradley force field (UBFF)[14–17] or an orbital valency force field (OVFF).[18] However, average frequency deviations of about 15 cm^{-1} result when all the frequencies are used. This unsatisfactory result reflects both the perturbations on octahedral symmetry and the intrinsic inadequacy of these force fields for the BiX_6^{3-} systems. However, since aqueous solution Raman spectra have been obtained for the X = Cl, Br, and I ions (unperturbed) and since a scheme has been devised to determine the UBFF constants from the Raman frequencies ν_1, ν_2, and ν_5, we have carried out these calculations. The results are shown in Table X.[19] Due to the approximations made the absolute values do not have much significance, but it is clear that the stretching force constants K are quite small (vs. values of about 4 mdyn/Å for fifth-row hexafluorides).

The most meaningful comparison of force constants can be obtained by considering the symmetric and antisymmetric frequencies for each type of bismuth–halogen group in each complex. These are assumed to be uncoupled to the other vibrational modes and are used to calculate the valence force field stretching (f_R) and interaction (f_{RR}) constants. For example, the $BiBr_5^{2-}$ has three types of $BiBr_2$ groups as can be seen in Figure 1. The types of groups (external or bridging) along with the nature of the trans halogens are listed in Table XI as are the frequencies and force constants calculated from them. Thus, for the $BiBr_5^{2-}$ species f_R and f_{RR} are calculated for the two external types of $BiBr_2$ groups by using the assigned symmetric and antisymmetric stretching frequencies. For the bridged $BiBr_2$ group only one averaged value for the stretching frequency is used to calculate an approximate f_R.

This same type of calculations has been carried out for each of the other halobismuthate ions and the results are shown in Table XI. As expected, the force constants for external bond stretches are higher than those for the bridging ones, and Bi–Br bonds are stronger than Bi–I bonds (except in the BiX_6^{3-} complexes where the force constant values are similar). In addition, however, some interesting trends were observed. For one, bonds trans to external halogens were weaker than those trans to bridging halogens. Apparently a sort of "trans effect" is occurring where a more strongly bound group tends to limit the amount of electron density available for the bonding at the position trans to itself. Thus, the force constants for external Bi–Br stretches having trans bridging groups range from 0.95 to 1.12 mdyn/Å while those with trans external groups range from 0.69 to 0.88 mdyn/Å. For Bi–I stretches the comparison is 0.77–0.87 mdyn/Å for bonds trans to bridging groups vs. 0.70 mdyn/Å for those trans to external groups. Similar weakening of bonds trans to ligands showing strong trans influence has been observed a number of times previously, primarily for transition-metal complexes, and vibrational spectroscopy has been invaluable in demonstrating this "trans effect".[20] A second observation also confirms the fact that external halogens use up more electron density on the bismuth atom than do bridging halogens and thereby weaken the bonds to other halogen atoms. In the $BiBr_6^{3-}$ anion in which all the Bi–Br bonds are external, the stretching force constant is 0.69 mdyn/Å. In the $BiBr_5^{2-}$ complex, which has two bridging halogens, the similar bond has a constant of 0.88 mdyn/Å. Comparison of external Bi–Br stretching constants for bonds trans to bridging groups shows them increasing from 0.95 to 0.97 to 1.12 mdyn/Å in going from complexes with two bridged halogens to those with three and then four bridged halogens. Exactly the same trend occurs for the iodobismuthates. Consequently, the highest stretching frequencies and force constants exist for the external Bi–X bonds in the BiX_4^- complexes which have the largest number of bridging halogens. The lowest frequencies and constants exist for the BiX_6^{3-} octahedral complexes which have only externally bonded halogens, all of which are competing strongly for the electron density.

A final observation on the force constant values is that the interaction f_{RR} is about 0.3 mdyn/Å for trans interactions in both the bromo and iodo complexes, while f_{RR} is 0.1 mdyn/Å or less for cis interactions. This again clearly reflects the trans effect since higher positive values for the interaction constants result from the increased difficulty in simultaneously stretching two Bi–X bonds.

Conclusions

This study has established the characteristic features of the vibrational spectra for seven different bromobismuthate and iodobismuthate anions. It was observed that the far-infrared and Raman spectra (especially the latter) can be used to determine which ion is present in a particular complex. Moreover, it was found that the spectra fit nicely with prediction for the known bromobismuthate structures (from

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X-ray) and strongly support the notion that the iodobismuthates have analogous structures. It is quite apparent that bridged structures do exist for BiX_5^{2-}, $Bi_2X_9^{3-}$, and BiX_4^- complexes and that no lone pairs are present.

The analysis of the force constants determined from the stretching frequencies demonstrated an interesting competition between the different halogen atoms for the electron density on bismuth required for bonding. Bridged halogens, which form weaker Bi–X bonds than external halogens, utilize less electron density and allow the other bonds in their complexes, especially those trans to them, to be proportionally stronger. Previous studies[20] on systems such as $[PtCl_3X]^-$, $Pt(PEt_3)_2(H)X$, and $Ru(NH_3)_4(NO)X$ have shown decreases in $\nu(PtCl)$, $\nu(PtH)$, and $\nu(RuNO)$ frequencies with increasing trans effect of the X group. Since the trans influence for halogens is in the order $Cl < Br < I$, it is not surprising to see a similar effect for the bromo- and iodobismuthates. These ions are unique, however, in that the relative magnitude of the observed trans influence is determined not only by which atoms are trans to a particular group but also by whether these atoms are bridged or external. The observed trans influence from this study shows Br(bridged) < Br(external) and I(bridged) < I(external). We have also carried out similar studies on haloantimonates,[21] but the trans effect in these ions is less pronounced. This probably reflects the fact that the smaller antimony atom is less polarizable and thus less susceptible to trans influences.

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Registry No. $BiBr_6^{3-}$, 15978-03-7; $(CH_3NH_3)_3BiBr_6$, 29532-34-1; $(C_6H_5CH_2NH_3)_3BiBr_6$, 29532-27-2; $(n\text{-}C_3H_7NH_3)_3BiBr_6$, 29532-31-8; $(C_3H_5NH_3)_3BiBr_6$, 29532-28-3; (4-picolinium)$_2$BiBr$_5$, 71733-94-3; (pyridinium)$_2$BiBr$_5$, 71733-95-4; $(Et_3NH)_3Bi_2Br_9$, 30815-45-3; $(i\text{-}Bu_2NH_2)_3Bi_2Br_9$, 29532-24-9; (quinolinium)BiBr$_4$, 28961-38-8; (3-picolinium)BiBr$_4$, 28961-39-9; BiI_6^{3-}, 14636-73-8; $(n\text{-}C_3H_7NH_3)_3BiI_6$, 19478-43-4; $(Cr(en)_3)BiI_6$, 71733-85-2; $(Me_2NH_2)_3Bi_2I_9$, 12327-10-5; (piperidinium)$_3$Bi$_2$I$_9$, 69853-26-5; (4-picolinium)$_3$Bi$_2$I$_9$, 12327-81-0; $(n\text{-}C_3H_7NH_3)BiI_4$, 71733-86-3; $((CH_3)_2CHNH_3)BiI_4$, 71733-87-4.

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Ultraviolet Photoelectron Spectroscopy of Thiaboranes

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The He I and Ne I photoelectron spectra of 1-SB_9H_9, 1-$SB_{11}H_{11}$, 6-SB_9H_{11}, 10-CH_3-1-SB_9H_8, 10-Br-1-SB_9H_8, and 6-Br-1-SB_9H_8 as well as the He I spectra of 1,10-$C_2B_8H_{10}$, 1,12-$C_2B_{10}H_{10}$, and $B_{10}H_{14}$ are reported. Observed band characteristics allow a qualitative description of the highest occupied molecular orbitals of 1-SB_9H_9 to be developed. Parameterization of the observed substitution effects defines the availability of electron density at the 6- and 10-positions of 1-SB_9H_9 relative to other borane frameworks.

In past work we have demonstrated that UV photoelectron spectroscopy can be used effectively to empirically characterize the electronic structure of small boranes and heteroboranes.[2] This technique yields an exact, but not very detailed, description of the lowest lying radical cation states which can be translated into a description of the occupied molecular orbitals of the molecule.[3] Further, the examination of substituted boranes has revealed the nature of the perturbation of framework orbitals by cage substituents.[4,5] Here we extend this work to some large frameworks, particularly those containing sulfur as the heteroatom.

Recent investigations have shown that thiaborane structures[6] are reminiscent of borane and carbaborane frameworks and appear to be predictable by electron-counting systematics.[7] The directive effects of the sulfur in the electrophilic substitution reactions of 1-SB_9H_9 and $SB_{11}H_{11}$ have also been defined.[8,9] Initial substitution does not appear to correlate with the ground-state charge distribution as apparently is the case with the carbaboranes. Also, the first facile hydroboration reaction by a polyhedral borane was recently demonstrated for 6-SB_9H_{11}.[10] Thus, it seems that the sulfur heteroatom imparts a unique chemistry to thiaboranes.

Results and Disscussion

Model. The equatorial–apex model used below to discuss the spectra is described by Hoffmann and Lipscomb.[11] In it the orbital structure of the cage is generated from the orbitals of one equatorial and two apical fragments. The advantage of a fragment model such as this is that many oribtals are essentially transferable between different molecules containing the fragment.[12] The model is not exact, however, and is used here simply as a language to facilitate the discussion of the

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