The Opaque Rutile Phase. The magnetic susceptibility of the opaque rutile phase was measured from 4.2 to 300 K. No remnant moment was found at 4.2 K. In Figure 4, χ^{-1} vs. T of the opaque phase is compared with that of VF_2. In calculating χ^{-1} for this plot, the formula weight of VF_2 was used for the opaque phase. From the plot, one sees the slope of the opaque phase is greater than that of VF_2, indicating a smaller average magnetic moment per unit mass. This is consistent with the conclusion that the opaque material has stoichiometry close to VF_2 but between VF_2 and VF_3. The formula for the opaque phase should therefore be written $VF_{2+\delta}$ ($V^{II}_{1-\delta}V^{III}_{\delta}F_{2+\delta}$). Assuming the orbital moment of V^{3+} is quenched and average g values of 1.97 and 1.80[8] for VF_2 and VF_3, respectively, we can make an estimate of δ. The theoretical Curie constants for V^{2+} and V^{3+} should be $C_{(2+)} = 1.82$ and $C_{(3+)} = 0.81$. The Curie constant of $VF_{2+\delta}$, calculated from the paramagnetic region of the χ^{-1} vs. T plot, is 1.76. Since $C_M = (1 - \delta)C_{(2+)} + \delta C_{(3+)}$, a first approximation value for δ is 0.06. A second approximation is obtained by replotting χ^{-1} vs. T of $VF_{2+\delta}$ using the formula weight of $VF_{2.06}$. This gives values of $C_M = 1.78$ and $\delta = 0.04$. The value 0.04 may still be high as a consequence of possible contamination by finely divided VF_3. At any rate, δ is small and would be difficult to establish by conventional chemical analysis.

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Registry No. VF_2, 13842-80-3; MgF_2, 7783-40-6; $MgVF_4$, 71749-59-2; $Li_{0.50}VF_3$, 56092-96-7.

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Coordination Compounds of Indium. 34. Preparative and Spectroscopic Studies of InX_3Y^- and $InX_2Y_2^-$ Anions ($X \neq Y$ = Cl, Br, I)

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The oxidation of indium(II) complexes $In_2X_6^{2-}$ (X = Cl, Br, I) with halogen (Y_2; Y = Cl, Br, I) yields the anionic mixed-halogeno complexes InX_3Y^-. Similar oxidations of the indium(I) anions InX_2^- furnish $InX_2Y_2^-$ anions, all as salts with tetraalkylammonium cations. The far-infrared and Raman spectra establish that the anions are indeed the mononuclear mixed-ligand species, and force constant calculations, using a modified valence force field method, confirm the vibrational assignments. The reaction mechanism and some trends in the force constants are discussed.

Introduction

In a recent paper,[1] the preparation of the first unambiguous indium(II) complexes was reported, in the form of the salts tetrabutylammonium hexahalogenodiindate(II). Vibrational spectroscopy and some simplified force constant calculations showed that these anions contain an indium–indium bond linking two InX_3^- units. We have now begun to investigate the chemical properties of these substances. One obvious reaction is oxidation, in which one might expect cleavage of the indium–indium bond to give X_3InY^- compounds. By way of a preliminary study of the generality of such reactions, we have carried out the oxidation of all three $In_2X_6^{2-}$ anions with other halogens in benzene to give the anionic mixed-halogeno complexes InX_3Y^-. At the same time, the availability of InX_2^- salts[2] allowed us to study the oxidation of these compounds under similar conditions, when the products are $InX_2Y_2^-$ anions. The preparation of these compounds and the infrared and Raman spectra to 50 cm^{-1} are now reported, together with some force constant calculations which serve to establish that the products are indeed the anions in question.

There have been no previous reports on the preparation or properties of such mixed-halide complexes of indium, but several anionic complexes in which thallium(III) is bonded to two different halides have been reported. Preparative work,[3,4] vibrational spectroscopy,[4,5] electronic spectroscopy,[6] and X-ray powder methods[6] have established the existence of these mononuclear complexes, although there is some dispute as to whether or not dissociation in solution gives rise to mixtures of the appropriate TlX_4^- and TlY_4^- anions.[5,6]

Experimental Section

Starting Materials (General). The tetra-*n*-butylammonium salts of hexahalogenoindate(II) anions were prepared via InX_2 as described in the previous paper.[1] Tetraethylammonium salts of dihalogenoindate(I) anions were obtained from the reaction of the appropriate $(C_2H_5)_4NX$ + HX species with cyclopentadienylindium(I).[2]

Solvents and analytical methods were as in the previous work.[1,2]

Preparations. (a) $InCl_3I^-$, $InBr_3I^-$, $InCl_3Br^-$, InI_3Br^-, $InCl_2I_2^-$, $InBr_2I_2^-$. Weighted quantities (approx 2 mmol) of bromine and iodine were dissolved in benzene (50 cm^3), the solution was heated to boiling, and the calculated amount of the appropriate $((C_4H_9)_4N)_2In_2X_6$ or $((C_2H_5)_4N)InX_2$ salt was added in small portions over about 5 min. The color of the halogen discharged progressively during the addition, and the final colorless solution was allowed to cool to room temperature, when a brownish oil settled out. The benzene layer was decanted and the oil taken up in hot ethanol (20 cm^3); the solution was filtered hot and allowed to crystallize on cooling.

(b) $InBr_3Cl^-$, InI_3Cl^-, $InBr_2Cl_2^-$. A solution of chlorine in benzene was prepared, and the concentration was determined titrimetrically with $Na_2S_2O_3$ after addition of excess KI. Calculated quantities of salts of $In_2X_6^{2-}$ (X = Br, I) or $InBr_2^-$ were then added to approximately 50 cm^3 of a solution containing 2–4 mmol of Cl_2 at room temperature, and the product was isolated as described above.

The order of addition of reagents was found to be critically important, since if one adds a halogen Y_2 to a solution of

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Table I. Melting Points and Analytical Results for $[(C_4H_9)_4N]InX_3Y$ and $[(C_2H_5)_4N]InX_2Y_2$ Salts

anion	mp, °C	% found		% required	
		In	halogen[a]	In	halogen[a]
$InCl_3Br^-$	128	21.0	34.2	21.1	34.3
$InCl_3I^-$	109–111	19.3	39.9	19.4	39.5
$InBr_3Cl^-$	128–130	17.9	43.3	18.2	43.5
$InBr_3I^-$	118–120	15.6	50.5	15.9	50.7
InI_3Cl^-	122–124	14.7	53.6	14.9	53.8
InI_3Br^-	125	14.1	56.3	14.0	56.3
$InCl_2Br_2^-$	288	24.5	48.3	24.1	48.5
$InCl_2I_2^-$	246	20.2	57.1	20.2	57.0
$InBr_2I_2^-$	289	17.4	63.0	17.4	62.8

[a] Expressed as % X + % Y in each case.

$((C_4H_9)_4N)_2In_2X_6$ in benzene, precipitation of the XY_2^- salt occurs more quickly than the redox reaction. This was demonstrated specifically in the simplest case, namely, $((C_4H_9)_4N)_2In_2I_6 + I_2$, when the precipitated $(C_4H_9)_4NI_3$ was collected and identified. The significance of this result in terms of the reaction mechanism is discussed later.

The procedures described gave yields of crystalline products in the order of 60–80%. Analytical results and uncorrected melting points are given in Table I.

Spectroscopic Techniques. Far-infrared spectra were recorded on a Perkin-Elmer 180 spectrometer operating in conjunction with an Interdata Model 6/16 computer for data accumulation and curve smoothing. The samples were run as Nujol mulls between polyethylene plates. The polyethylene peak at 70 cm^{-1} was subtracted out by the "difference" routine in the program, thereby permitting identification of vibrations in this region. Raman spectra were recorded on a Spectra-Physics Model 700 spectrometer using argon-ion excitation. The compounds are not soluble in nonpolar solvents, and spectra recorded in methanol or acetonitrile solution differed significantly from those of the solid, suggesting a change in structure on dissolution, and we were therefore unable to record reliable polarization data.

Force Constant Calculations. Normal-coordinate calculations were carried out on an IBM S/360-65 series computer using the program LARMOL (I).[7] The In–X bond lengths were assumed to be the same as in related anionic indium–halide complexes.[8]

Results and Discussion

Preparations. The preparation of the mixed-ligand complexes InX_3Y^- and $InX_2Y_2^-$ from indium(II) and -(I) starting materials confirms the view expressed earlier[9] that such low-oxidation compounds do indeed permit syntheses which cannot be readily carried out with indium(III) compounds. The use of the reaction $In_2X_6^{2-} + Y_2 \rightarrow 2InX_3Y^-$ is now being investigated with Y_2 species of greater complexity than the halogens.

The vibrational spectra and more especially the force constant calculations discussed below show that the products are indeed the mononuclear mixed-ligand species and not mixtures of (say) $3InX_4^- + InY_4^-$. Thus the method of preparation and perhaps in particular the use of benzene as a solvent from which the products quickly precipitate apparently prevent significant redistribution via equilibria of the type

$$4InX_3Y^- \rightleftharpoons 3InX_4^- + InY_4^- \qquad (1)$$

This is a useful conclusion in itself, given the known tendency of indium(III) species to undergo rapid rearrangement in polar solvents.[10]

The stoichiometrically simple reaction

$$In_2X_6^{2-} + Y_2 \rightarrow 2InX_3Y^- \qquad (2)$$

describes the stoichiometry of the principal reaction, but it appears that there are both experimental and theoretical reasons for believing that the reaction does not involve the flow of electrons from $In_2X_6^{2-}$ to Y_2. Electron transfer in such a concerted process would be from the HOMO of the In_2 bond to LUMO of Y_2, but the molecular orbitals involved in the In–In bond are of g symmetry, as opposed to the u symmetry in the LUMO level of Y_2, implying that the reaction cannot be concerted. This argument is reinforced by the side products which are found in some cases (see below) and by studies of various analogous reactions.[11–14]

The precipitation of R_4NX_3 salts when a solution of halogen is added to a suspension of the $In_2X_6^{2-}$ salt (see Experimental Section) points to the existence of a competing reaction, namely

$$In_2X_6^{2-} + 2Y_2 \rightarrow In_2X_4 + 2XY_2^- \qquad (3)$$

The indium(II) halides are known to be soluble in aromatic solvents,[15] whereas X_3^- salts are demonstrably not. In fact, the preparative work involved the reverse procedure, namely, the addition of solid $In_2X_6^{2-}$ salt to a solution of Y_2, which is therefore present in local excess over the dissolving salt, and under these conditions the formation of InX_3Y^- will predominate. If the cleavage of the In–In bond in (3) is slow or if the In···In···Y···Y association is weak, then formation of XY_2^- may become significant.

One other important side reaction should be noted, since this relates to the possible formation of $InX_2Y_2^-$ in those cases where the primary product is InX_3Y^-. These species could arise by the sequence

$$In_2X_6^{2-} \rightleftharpoons InX_2^- + InX_4^- \qquad (4)$$

$$InX_2^- + Y_2 \rightarrow InX_2Y_2^- \qquad (5)$$

Equilibrium 4 was proposed in earlier work to explain certain preparative results,[1] and as with other equilibria involving indium halides, the equilibrium distribution is apparently solvent dependent. While it appears to lie strongly to the left in aromatic solvents at room temperature, small quantities of InX_2^- may well be present under our experimental conditions (80 °C) and could lead to the formation of $InX_2Y_2^-$ by reaction 5.

In summary then, the reactions in the $In_2X_6^{2-}$ systems are more complex than initially expected, but the analytical results (Table I) and spectra show that the impurities are apparently present in only small quantities. The reactions of InX_2^-, on the other hand, are apparently straightforward addition reactions, since no impurities are detected except in the case of $InCl_2^-/I_2$. (See below.)

Vibrational Spectra and Normal-Coordinate Analysis of InX_3Y^- Anions. The vibrational representation of an InX_3Y^- anion is $\Gamma_v = 3\ A_1 + 3\ E$. The three A_1 modes are designated as $\nu_s(InX_3)$, $\nu_s(InY)$, and the symmetric deformation, while the three E modes are $\nu_d(InX_3)$, $\delta_d(InX_3)$ [XInX scissors], and ω_d [wagging of the Y atom perpendicular to the InX_3 axis] (s = symmetric, d = degenerate).

The observed infrared and Raman spectra of the various InX_3Y^- anions are given in Table II, together with the calculated frequencies and potential energy distributions. The tables also list the various bands not assignable to these anions (see below). It is as well to point out that in this table there are some possible ambiguities, exemplified by the fact that ν_4

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Table II. Vibrational Spectra of InX_3Y^- Anions (in cm^{-1})

assignt		obsd			
A_1	E	IR	Raman	calcd	PED[a]
		(a) $InCl_3Br^-$			
	ν_4	330 s		335	103 (1) − 5 (8)
ν_1		320 s, sh	320 vs	320	81 (1) + 10 (2) + 8 (8)
ν_2		237 ms	258 w (?)		
		228 ms	226 s	228	11 (1) + 84 (2)
		218 m			
	ν_5	113 ms	108 sh	113	98 (4)
ν_3		103 ms		104	52 (4) + 36 (7) + 5 (11)
	ν_6	80 w, br	74 w	79	99 (7)
		(b) $InCl_3I^-$			
	ν_4	330 s		334	103 (1) − 4 (8)
ν_1		315 m, sh	320 s	318	87 (1) + 4 (3)
		192 mw			see text
ν_2		185 s	184 w	183	5 (1) + 87 (3)
		170 w	166 w		see text
	ν_5	114 s		111	97 (4)
ν_3		100 m, sh		95	44 (4) + 24 (7) + 18 (3) + 15 (11)
	ν_6	65 w		73	101 (7) − 4 (11)
		(c) $InBr_3Cl^-$			
ν_1		325 s	318 m	321	93 (1) + 4 (2)
	ν_4	225 s	229 m	228	99 (2) − 7 (9)
ν_2		206 s	197 s	195	81 (2) + 11 (9)
	ν_5	104 m		98	6 (2) + 92 (7)
		90 m			(?)
ν_3		85 m		85	46 (7) + 43 (5) + 7 (11)
	ν_6	ca. 70		69	96 (5)
		(d) $InBr_3I^-$			
	ν_4	226 s	230 m	230	95 (2)
		212 s	215 m		see text
ν_1		191 ms	194 vs	192	50 (2) + 42 (3)
ν_2		168 m	166 vs	168	36 (2) + 50 (3)
		158 sh	156 sh		see text
			139 vw		see text
	ν_5	76 ms	73 m	73	93 (5)
ν_3		60 sh		65	54 (5) + 37 (7)
	ν_6	50 w	53 m, sh	53	96 (7)
		(e) InI_3Cl^-			
		320 m, sh			see text
ν_1		312 m	305 mw	305	95 (1)
	ν_4	186 s	186 vs	186	97 (3) − 9 (10)
		181 s			
ν_2			147 m, sh	147	78 (3) + 4 (1) + 14 (10)
			132 s		
	ν_5	ca. 70 m, br		80	10 (3) + 89 (7)
ν_3		65 m		65	40 (7) + 36 (6) + 18 (11)
		60 m, sh (?)			
	ν_6	45 w		45	97 (6) − 5 (11)
		(f) InI_3Br^-			
		225 s, sh			see text
ν_1		216 s	214 m	215	71 (2) + 18 (3) + 5 (10)
	ν_4	183 vs	187 s	185	104 (3) − 15 (10)
		158 vw	155 m, br, sh		(?)
ν_2		145 vw	139 vs	140	26 (2) + 58 (3) + 16 (10)
	ν_5	64		65	10 (3) + 88 (7)
		61			
ν_3				60	50 (7) + 37 (6) + 7 (11)
	ν_6	45 (?)		45	94 (6)

[a] PED = potential energy distribution.

is the degenerate InCl stretch in $InCl_3Br^-$ and $InCl_3I^-$, the degenerate InBr stretch in $InBr_3Cl^-$, and the degenerate InI stretch in InI_3Cl^- and InI_3Br^-. An approximate description of each mode is therefore included on the extreme right-hand column of the table in terms of the force constants listed in Table IV. The assignments have been made by comparing anions with common InX_3 and InY groups and with the established assignments for InX_4^- anions.[16-19]

In general the far-infrared spectra of the InX_3Y^- and $InX_2Y_2^-$ species show broad bands, and the deformation bands in the region of 70 cm^{-1} are partially obscured by the polythene band at this frequency, although this problem can be solved by computation (see Experimental Section). The Raman spectra confirm the infrared stretching frequencies, but again

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some of the deformation modes near the exciting line are poorly defined. Fortunately, enough of the modes are observed to allow those in doubt to be estimated from the force constant calculations. Equally, sufficient features are unambiguously established to show that the compounds are indeed salts of (e.g.) InX_3Y^- anions. In the subsequent analysis, the anions are assumed to be sufficiently separated by the large tetra-*n*-butylammonium cations that intermolecular coupling of vibrational motions can be safely ignored. Reasonable assignments can then be made on the assumption that local C_{3v} symmetry is operative for the InX_3Y^- species.

The frequencies reported by Woodward et al.[16-18] were used to calculate force constants for the InX_4^- species (X = Cl, Br, I) by our program. These preliminary results provided a check on the calculations and gave force constants in good agreement with previous work based on a general quadratic valence force field.[19] In the latter study, the problem of having more force constants than fundamentals was overcome by equating $f_{r\alpha}$ and $f_{\alpha'}$ following the procedure of Donaldson et al.[20] The values for the InX_4^- species in Table IV do not differ by more than 1–2% from those reported previously.[19]

The assigned frequencies of $InCl_3Br^-$ are given in Table IIa. The $InCl_3$ stretching modes ν_d and ν_s are straightforwardly assigned to 330 and 320 cm^{-1}, respectively. Three bands, at 237, 228, and 218 cm^{-1}, are observed in the expected region of ν_s(InBr), instead of the predicted singlet; we suggest that is due to Fermi resonance between $2\nu_3$ and/or $2\nu_5$ and assign the fundamental ν_2 to the average value of 228 cm^{-1}. The degenerate and symmetric δ(ClInCl) bending modes are placed at 112 and 103 cm^{-1}, respectively, corresponding to δ_d in $InCl_4^-$ at 112 cm^{-1}, leaving the ClInBr bend to be assigned to the weak band at 80 cm^{-1}.

In $InCl_3I^-$ (Table IIb), the modes assignable to the $InCl_3$ moiety are almost unchanged from those in $InCl_3Br^-$. The In–I symmetric stretch, which occurs with medium intensity in the infrared and is strong in the Raman spectrum, is placed at 185 cm^{-1}. The degenerate δ(ClInI) deformation is predicted to be very close to 70 cm^{-1}, and a weak feature is apparent in the spectra at ca. 65 cm^{-1}. Weak features in the IR spectrum at 192 and 170 cm^{-1}, and at 168 cm^{-1} in the Raman, cannot be accommodated in this scheme, and we believe that these bands indicate the presence of small quantities of $InCl_2I_2^-$ + $InCl_4^-$ in the product. These are the only vibrations of such a mixture which would not be coincident, or nearly so, with the bands of $InCl_3I^-$. The routes by which these impurities could have been formed were discussed earlier.

For the species InI_3Cl^- (Table IIe) and InI_3Br^- (Table IIf), in which the InX_3 group involves the heaviest halogen, the assignments to fundamentals which correspond to motions of the InI_3 group are very similar in both cases. The symmetric InI stretches are at 147 and 140 cm^{-1} and degenerate stretches at 185 and 186 cm^{-1}. The degenerate δ(IInI) bending mode is at 45 cm^{-1} in both molecules, while the corresponding symmetric bending modes are slightly higher at 65 and 60 cm^{-1} in the chloride and bromide, respectively. The ClInI deformation (at 80 cm^{-1}) is higher than the δ(BrInI) deformation (estimated at 65 cm^{-1}), as expected on the basis of relative mass. In both systems, high-energy shoulders suggest some slight contamination of the product by the appropriate $InX_2Y_2^-$ anion (see discussion below in terms of $InBr_3I^-$).

The assignment of the spectrum of $InBr_3Cl^-$ (Table IIc) is relatively straightforward, based on comparisons with the other mixed species and with $InBr_4^-$, with the calculations supporting the line coinciding with the polyethylene band at 70 cm^{-1}. The case of $InBr_3I^-$ is more difficult, since there are more bands in the spectrum than can be accounted for in terms of this anion alone. The assignments in Table IId were made by comparison with other InX_3Y^- anions, with calculated frequencies based on reasonable values for the force constants. In this way, the antisymmetric and symmetric $\nu(InBr_3)$ stretches are placed at 230 and 194 cm^{-1} and the degenerate δ(BrInBr) at 76 cm^{-1} (cf. analogous bands at 225, 205, and ca. 70 cm^{-1} in $InBr_3Cl^-$). The bands at 60 (shoulder) and 50 cm^{-1} present in both infrared and Raman spectra are assigned to ν_3 and ν_6, respectively. This then leaves the InI stretching mode to be assigned, with bands at 168 (vs), 156 (m, sh), and 139 (vw) cm^{-1} in the energy range expected for this vibration. The 168-cm^{-1} band is the strongest and the easiest to accommodate into the normal-coordinate calculation and is therefore assigned to ν_s(InI); placing this mode at either 139 or 156 cm^{-1} implies improbably low values for the InI stretching force constant. We believe that the extra bands are due to the disproportionation of $In_2Br_6^{2-}$ to $InBr_2^-$ and $InBr_4^-$, followed by reaction of $InBr_2^-$ to give $InBr_2I_2^-$ (cf. discussion earlier). One would then expect to see the various vibrations of $InBr_2I_2^-$ and $InBr_4^-$. Most of the vibrations of $InBr_2I_2^-$ are coincident, or nearly so, with those of $InBr_3I^-$, with the exception of ν_3 (149 cm^{-1}), and there is indeed a strong shoulder in the Raman spectrum of $InBr_3I^-$ at this frequency; the ν_9 band would be masked by ν_1 of $InBr_4^-$ (195 cm^{-1}). Similarly in the infrared, ν_3 of $InBr_4^-$ (239 cm^{-1}) would be in the broad envelope centered at 230 cm^{-1} (ν_4 of $InBr_3I^-$).

Table III. Vibrational Spectra of $InX_2Y_2^-$ Anions (in cm^{-1})

assignt		obsd			
A_1	B	IR	Raman	calcd	PED
(a) $InCl_2Br_2^-$					
	ν_6	328 s	328 sh	330	101 (1)
ν_1		325 sh	320 m	320	88 (1) + 8 (2)
	ν_7	236 vs	230 sh	233	100 (2) + 6 (7) − 7 (9)
ν_2		210 m	206 m	205	9 (1) + 81 (2) + 5 (9)
ν_3		105 m		105	82 (4) + 12 (7)
	ν_8	94 sh		90	89 (7) + 7 (2)
ν_4		*a*		84	96 (7)
	ν_9	82 m	80 ms	82	103 (7) − 5 (12)
ν_5				74	17 (7) + 82 (5)
(b) $InCl_2I_2^-$					
	ν_6	322 s	320 sh	320	103 (1)
ν_1		310 sh	313 s	314	90 (1) + 7 (3)
	ν_7	187 m	184 s	188	97 (3) + 15 (7) − 14 (10)
ν_2		167 mw	167 s	168	6 (1) + 74 (3) + 10 (10)
ν_3		105 m		101	78 (4) + 15 (7) + 8 (3)
	ν_8	~90 sh		86	73 (7) + 20 (3) + 10 (12)
ν_4		*a*		83	88 (7) + 12 (12)
	ν_9	~80 sh		76	114 (7) − 16 (12)
ν_5		50 m		54	82 (6) + 18 (7)
(c) $InBr_2I_2^-$					
	ν_6	229 s	230 sh	229	103 (2) − 8 (9)
ν_1		215 m	219 m	215	59 (2) + 27 (3)
	ν_7	187 s	188 s	187	106 (3) + 10 (7) − 16 (10)
ν_2		149 vw	149 vs	147	35 (2) + 54 (3) + 8 (10)
ν_3		77		70	81 (5) + 9 (7)
	ν_8	65 sh		62	90 (7) + 11 (3)
ν_4		*a*		60	5 (2) + 96 (7)
	ν_9	51 m		54	99 (7)
ν_5		48 sh (?)		48	23 (7) + 75 (6)

[a] The calculation indicated that this frequency is the (A_2) IR-inactive mode.

$InX_2Y_2^-$ Anions. The spectra of all the $InX_2Y_2^-$ species (X $\neq$ Y = Cl, Br, I) can be assigned on the basis of C_{2v} symmetry (Table III). Eight (4 A_1, 2 B_1, and 2 B_2) of the nine fundamentals are both Raman and infrared active, while the A_2 mode is active only in the Raman mode. The assignments are made initially on the basis of group characteristics. Thus, the three vibrations characteristic of the $InCl_2$ moiety are readily identified. The strongly infrared active band to highest

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(20) J. F. Donaldson, J. F. Knifton, J. O'Donaghue, and S. D. Ross, *Spectrochim. Acta*, **22**, 1173 (1966).

Table IV. Force Constants for InX_3Y^- and $InX_2Y_2^-$ Ions[a]

no.	descriptn	$InCl_3Br^-$	$InCl_2Br_2^-$	$InBr_3Cl^-$	$InCl_3I^-$	$InCl_2I_2^-$	InI_3Cl^-	$InBr_3I^-$	$InBr_2I_2^-$	InI_3Br^-	InX_4^-
1	In-Cl	1.72	1.65	1.59	1.68	1.58	1.45				1.89
2	In-Br	1.46	1.36	1.32				1.23	1.14	1.06	1.60
3	In-I				1.16	1.12	1.05	1.15	1.10	1.04	1.20
4	Cl-In-Cl	0.089	0.084		0.088	0.082					0.087
5	Br-In-Br		0.077	0.068				0.075	0.073		0.078
6	I-In-I					0.057	0.048		0.051	0.045	0.057
7	X-In-Y	0.060	0.064	0.082	0.055	0.062	0.077	0.050	0.054	0.069	
8	In-Cl/In-Cl	0.079	0.034		0.073	0.059					
9	In-Br/In-Br		0.092	0.097				0.094	0.078		
10	In-I/In-I					0.090	0.091		0.098	0.099	
11	XInX/XInY	−0.0020		−0.0022	−0.0073		−0.0062	−0.0032		−0.0034	
12	XInY/XInY		−0.004			−0.008			−0.004		

[a] Units: stretching, mdyn Å^{-1} (μN pm^{-1}); bending, values have been divided by $(r_{InX} \cdot r_{InY})^{1/2}$.

wavenumber is clearly the antisymmetric $InCl_2$ stretch at 328 cm^{-1} in $InCl_2Br_2^-$ (see Table IIIa) and at 320 cm^{-1} in $InCl_2I_2^-$ (see Table IIIb), with the corresponding distinct bands in the Raman spectra at 320 and 313 cm^{-1} being the symmetric $\nu_{a_1}(InCl_2)$ modes. The symmetric $\delta_{a_1}(InCl_2)$ bend is undoubtedly the band at ca. 105 cm^{-1} in both spectra. The corresponding three characteristic vibrations for the $InBr_2$ group can similarly be identified as the $\nu_b(InBr_2)$ mode at 236 and 229 cm^{-1}, the $\nu_{a_1}(InBr_2)$ mode at 206 and 215 cm^{-1}, and the $\delta_{a_1}(InBr_2)$ mode at 74 and 77 cm^{-1}, respectively, in $InCl_2Br_2$ and $InBr_2I_2$ (Table IIIa,c). The latter vibration is, of course, very close to the band in polyethylene, but the difference routine makes it clear that there is indeed an absorption at this frequency. Furthermore, the characteristic bands of the InI_2 group show up as the $\nu_b(InI_2)$ mode at 187 cm^{-1} (in both cases), the $\nu_{a_1}(InI_2)$ at 167 and 149 cm^{-1}, and the $\delta_{a_1}(InI_2)$ mode at 52 and 48 cm^{-1}, respectively, in $InCl_2I_2^-$ and $InBr_2I_2^-$. The remaining three modes, involving the motion of two different halides in each $(InX_2Y_2)^-$ molecule ion include the torsional mode, ν_{a_2}, which is only Raman active and not observed in the infrared spectra. The two remaining modes δ_{b_1} and δ_{b_2} are assigned to the peak in both the Raman and IR spectra of $InCl_2Br_2^-$ at 80 cm^{-1} and to a shoulder at 94 cm^{-1} in the IR spectrum, respectively. The corresponding modes in $InCl_2I_2^-$ are assigned to two shoulders at 80 and 90 cm^{-1} and in $InBr_2I_2^-$ to a distinct peak at 51 cm^{-1} and a shoulder at 65 cm^{-1}.

In $InCl_2I_2^-$, there is a weak feature in the spectra at ca. 155 cm^{-1} (w) (IR + Raman), which we suggest is evidence of I_3^- as a low-level impurity (cf. ν_3 of $I_3^- \approx 150$ cm^{-1}).[21] It is worth noting that the problems with impurity bands arise most closely in those systems where iodine is the oxidizing agent. Such problems apart, the vibrational spectral assignments appear to be unambiguous and confirm the conclusions of the preparative work.

Effect of Charge on Force Constants. As has already been indicated, a number of the assignments were based on the concept of a good fit with a reasonable set of force constants. The potential energy distributions and the descriptions of the modes in Tables II and III establish that most vibrations are well described by their conventional descriptions. An exception to this statement involves the anions $InBr_3I^-$, $InBr_2I_2^-$, and InI_3Br^-, since the ν_1 and ν_2 vibrations in each case show considerable mixing. The set of force constants in Table IV is self-consistent for all of the anions studied.

It has been pointed out previously[19] that the strength of the primary stretching force constant is dependent on the formal oxidation state of the central element in MX_3^{n-} complexes (M = In^I, Sn^{II}, Sb^{III}; X = Cl, Br, I) and that this finding is in keeping with an ionic-bonding model. We have now tested this idea in a different but related way by examining the dependence of the stretching force constant (f_{In-X}) upon the charge separation ($\delta_{In} - \delta_X$) calculated by the method of Huheey.[22] The force constants show some clear monotonic trend with charge separation; in general, as the number of lighter, more electronegative ligands increases, within a series, so do the stretching force constants increase. The values for the tetrahedral InX_4^- anions do not however fit with this analysis, and the deviations get increasingly large in the order I > Br > Cl. This may reflect some artifact in our treatment, and it is planned to carry out more sophisticated calculations on these and related systems in the future.

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Registry No. $[(C_4H_9)_4N]InCl_3Br$, 71785-24-5; $[(C_4H_9)_4N]InCl_3I$, 71749-61-6; $[(C_4H_9)_4N]InBr_3Cl$, 71749-62-7; $[(C_4H_9)_4N]InBr_3I$, 71749-64-9; $[(C_4H_9)_4N]InI_3Cl$, 71749-65-0; $[(C_4H_9)_4N]InI_3Br$, 71749-67-2; $[(C_2H_5)_4N]InCl_2Br_2$, 71749-69-4; $[(C_2H_5)_4N]InCl_2I_2$, 71749-71-8; $[(C_2H_5)_4N]InBr_2I_2$, 71749-73-0; $[(C_4H_9)_4N]_2In_2Cl_6$, 59643-22-0; $[(C_4H_9)_4N]_2In_2Br_6$, 59643-24-2; $[(C_4H_9)_4N]_2In_2I_6$, 59643-26-4; $[(C_2H_5)_4N]InCl_2$, 57586-95-5; $[(C_2H_5)_4N]InBr_2$, 57650-22-3; $[(C_2H_5)_4N]InI_2$, 57556-85-1.

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