

phen. On heating, the solid began to decompose over 200° in a sealed ampoule. Elemental analysis was that for GaBr₂(phen)-BF₄.

Interaction of Gallium Trihalides with Pyridine.—When a solution of 0.150 g (1.90 mmol) of pyridine in 10 ml of methylene chloride was added dropwise to a solution of 0.224 g (1.27 mmol) of gallium trichloride in 20 ml of methylene chloride, a highly vigorous reaction occurred. Upon evaporation of the solvent a white solid was obtained. This was recrystallized from acetonitrile-ether, filtered, and dried *in vacuo*. The resulting solid melts at 93–94°. This same product was obtained when varying ratios of pyridine and gallium trichloride were mixed in methylene chloride, although the melting points of the products were slightly different. The elemental analysis given in Table V is the average of three analyses of the complex and corresponds closely to the 2:3 GaCl₃:py mole ratio.

When excess pyridine was added to gallium tribromide solution in methylene chloride, a vigorous reaction occurred. Evaporation of the solvent left a white solid, which was recrystallized from methylene chloride. Elemental analysis (Table V) corresponds to the 1:2 GaBr₃-py complex, mp 83–84° (lit. mp²⁷ 88°). In other attempts, addition of pyridine solutions in methylene chloride to gallium tribromide in the same solvent in the mole ratio of 1:1 or 2:1 pyridine-gallium tribromide resulted in the formation of white solids having melting points of 126–127 and 129–130°, respectively. The elemental analysis results (Table V) were very close and correspond to the 2:3 GaBr₃-py complex.

Similar experiments with gallium triiodide gave a white solid,

which turns yellow on standing for a few hours under vacuum and decomposes on heating to 180°. Elemental analyses were not satisfactory for any proposed composition.

All elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Because of the extreme moisture sensitivity of gallium trihalide-acetonitrile complexes, low halide contents were consistently obtained as a result of hydrolysis. A summary of elemental analyses is given in Table V.

The apparatus and procedure for conductance measurements have been described in detail.²⁵ The infrared spectra of Nujol mulls and thin films of solution were taken with a Beckman Model IR 10 spectrophotometer and a Perkin-Elmer Model 521 spectrophotometer made available by the University of Illinois. For mulls, CsBr and CsI windows were employed. Solution spectra were measured in a 0.1-mm solution cell provided with CsBr windows down to the 300-cm⁻¹ region and between polyethylene windows down to the 250-cm⁻¹ region.

Proton nmr spectra were obtained at 60 Mc using a Varian A-60 spectrometer equipped with a variable-temperature probe (V-6031) and a variable-temperature control unit (V-6040). The temperature was monitored by measuring the peak separation of methanol. The areas under the peaks were obtained by integration of the signals. Samples for nmr spectra were prepared by weight and all transfers were made in a dry nitrogen atmosphere. Because of the exothermic reaction, acetonitrile was added to the gallium tribromide samples cooled in liquid nitrogen.

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CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, SIMON FRASER UNIVERSITY, BURNABY 2, BRITISH COLUMBIA, CANADA, AND THE UNIVERSITY OF LEICESTER, LEICESTER LE1 7RH, ENGLAND

Coordination Compounds of Indium. X. Anionic Indium(III) Halide Complexes

By J. GISLASON,^{1a} M. H. LLOYD,^{1b} AND D. G. TUCK*^{1a}

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The compounds obtained from the reaction of substituted ammonium halides (CX) with indium(III) halides in organic solvents are shown to be salts of the type C[InX₄], C₂[InX₅], and C₃[InX₆]. Species of stoichiometry C₂InX₇ can be prepared, and the lattices of these apparently also contain InX₆³⁻ anions. Vibrational spectroscopy has been used to investigate the structures of the compounds prepared.

Introduction

Salts of anionic indium halide complexes were first reported a century ago,² and a number of species, such as K₃InCl₆ and NaInCl₄, have since been described in the literature.^{3–5} In 1936, Ekeley and Potratz⁶ found that reaction of an indium halide with the corresponding substituted ammonium or sulfonium halides in an organic solvent gives rise to a series of colorless crystalline compounds, which they formulated as double salts, but which are better written as the anionic indium complexes C[InX₄], C₂[InX₅], and C₃[InX₆]. Species with the stoichiometry C₂InX₇ were also reported (C = substituted ammonium or sulfonium cation). Crystal structure investigations have confirmed the formulation as anionic complexes^{7,8} for (C₂H₅)₄N[InCl₄] and ((C₂H₅)₄-

N)₂[InCl₅]. In addition a small number of substituted anionic indium halide complexes are known, although little structural information is available. The anion of the salt (NH₄)₂[InCl₅(H₂O)] has C_{4v} symmetry.⁹ Disubstituted anionic species, such as InCl₄L₂⁻ (L = urea, thiourea)¹⁰ and InCl₄bipy⁻ (bipy = 2,2'-bipyridyl),¹¹ have been prepared, but no X-ray structural investigations have been reported.

The object of the present work was to confirm and extend the preparative work on anionic indium halide complexes, to examine the vibrational spectra of these compounds, and to relate the findings to any relevant structural information. The Raman spectra of InX₄⁻ species in solution have been studied by Woodward and his coworkers,¹² and the vibrational spectrum of InCl₆³⁻ has been reported recently.¹³ While the

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TABLE I
 SALTS OF ANIONIC INDIUM(III) HALIDE COMPLEXES

	Analytical results, %				Mp, °C	Reaction medium
	Required		Found			
	In	Halogen	In	Halogen		
$(\text{CH}_3\text{NH}_2)_4\text{InCl}_7$	23.4	50.5	23.3	50.7	>230 subl	$\text{C}_2\text{H}_5\text{OH}$
$((\text{CH}_3)_2\text{NH}_2)_4\text{InCl}_7$	21.0	45.4	21.0	45.7	218	$\text{C}_2\text{H}_5\text{OH}$
$((\text{CH}_3)_3\text{NH})_3[\text{InCl}_6]$	22.6	41.9	22.5	41.7	184 dec	$\text{C}_2\text{H}_5\text{OH}$
$((\text{CH}_3)_4\text{N})_2[\text{InCl}_5]$	26.1	40.3	25.8	40.1	>300	CH_3OH
$((\text{C}_2\text{H}_5)_4\text{N})_2[\text{InCl}_5]$	20.8	32.1	20.7	32.3	285 dec	$\text{C}_2\text{H}_5\text{OH}$
$((\text{CH}_3)_3\text{C}_6\text{H}_5\text{N})_2[\text{InCl}_5]$	20.3	31.4	20.3	31.7	167	$\text{C}_2\text{H}_5\text{OH}$
$(\text{C}_6\text{H}_5\text{CH}_2(\text{C}_6\text{H}_5)_2[\text{InCl}_5]$	11.5	17.8	11.4	17.8	180	$\text{C}_2\text{H}_5\text{OH}$
$(\text{C}_2\text{H}_5)_4\text{N}[\text{InCl}_4]$	29.7	36.7	29.6	37.4	279	See text
$(n\text{-C}_3\text{H}_7)_4\text{N}[\text{InCl}_4]$	25.9	32.1	25.8	32.4	137	$\text{C}_2\text{H}_5\text{OH}$
$(\text{C}_6\text{H}_5)_4\text{As}[\text{InCl}_4]$	17.9	22.2	17.7	21.9	151	$\text{C}_2\text{H}_5\text{OH}$
$\text{Cs}_2[\text{InCl}_5(\text{H}_2\text{O})]$	19.9	30.8	19.8	31.0	>300	Concd HCl, 4 M HCl
$(\text{NH}_4)_2[\text{InCl}_5(\text{H}_2\text{O})]$	33.2	51.3	33.1	52.5	Dec	Concd HCl, 4 M HCl
$((\text{CH}_3)_4\text{N})_2[\text{InCl}_5(\text{H}_2\text{O})]$	25.0	38.7	24.9	38.6	>300	See text
$(\text{CH}_3\text{NH}_2)_4\text{InBr}_7$	14.3	69.7	14.3	69.5	228 dec	$\text{C}_2\text{H}_5\text{OH}$
$((\text{CH}_3)_2\text{NH}_2)_2\text{InBr}_7$	13.4	65.2	13.4	64.9	159	$\text{C}_2\text{H}_5\text{OH}$
$((\text{CH}_3)_4\text{N})_2\text{InBr}_5$	17.3	60.3	17.3	60.5	246	CH_3OH , $\text{C}_2\text{H}_5\text{OH}$
$(\text{CH}_3)_4\text{N}[\text{InBr}_4]$	22.6	62.8	22.2	62.9	...	4 M HBr
$(\text{C}_2\text{H}_5)_4\text{N}[\text{InBr}_4]$	20.3	56.6	20.4	56.5	299	$\text{C}_2\text{H}_5\text{OH}$
$(n\text{-C}_3\text{H}_7)_4\text{N}[\text{InBr}_4]$	18.5	51.5	18.5	51.2	139	$\text{C}_2\text{H}_5\text{OH}$
$(n\text{-C}_4\text{H}_9)_4\text{N}[\text{InBr}_4]$	17.0	47.2	17.0	47.1	131	$\text{C}_2\text{H}_5\text{OH}$
$\text{C}_6\text{H}_5(\text{C}_6\text{H}_5)_3\text{P}[\text{InBr}_4]$	15.2	42.4	15.2	42.3	71	$\text{C}_2\text{H}_5\text{OH}$
$(\text{NH}_4)_2[\text{InBr}_5(\text{H}_2\text{O})]$	20.1	70.3	19.5	70.9	201 dec	6 M HBr
$\text{Cs}_2[\text{InBr}_5(\text{H}_2\text{O})]$	14.4	50.1	14.4	50.1	...	6 M HBr
$(\text{CH}_3)_4\text{N}[\text{InI}_4]$	16.5	72.9	16.6	72.9	...	2 M HI
$(n\text{-C}_3\text{H}_7)_4\text{N}[\text{InI}_4]$	14.2	62.8	14.4	62.1	158	$\text{C}_2\text{H}_5\text{OH}$
$(n\text{-C}_4\text{H}_9)_4\text{N}[\text{InI}_4]$	13.3	58.7	13.4	58.3	135	$\text{C}_2\text{H}_5\text{OH}$
$\text{CH}_3(\text{C}_6\text{H}_5)_3\text{As}[\text{InI}_4]$	12.2	53.8	12.2	53.6	165	$\text{C}_2\text{H}_5\text{OH}$
$(\text{C}_6\text{H}_5)_4\text{As}[\text{InI}_4]$...	50.5	...	50.7	157	$\text{C}_2\text{H}_5\text{OH}$
$\text{Cs}[\text{InI}_4]$	15.2	67.2	15.0	67.0	...	2 M HI

present work was in progress, Shriver and Wharf^{14,15} published both solid- and solution-state infrared and Raman spectra of $((\text{C}_2\text{H}_5)_4\text{N})_2[\text{InCl}_5]$, and single-crystal studies of the vibrational spectra of this compound have recently been carried out.¹⁶ The preparation of some indium-chlorine complexes from aqueous solution¹⁷ and from melts¹⁸ has been reported by Atkinson and Field. The vibrational spectra of some neutral adducts of indium trihalides¹⁹ have been investigated, as have those of the parent trihalides.²⁰

Experimental Section

Spectroscopy.—Infrared spectra were obtained with Beckman IR-12 spectrophotometer or Research and Industrial Instruments Co. FS-620 Interferometer instruments. Raman spectra were run on a Cary-81 Raman spectrometer.

Preparations.—Table I lists the analytical and other results for the compounds discussed in this paper. Analytical data were obtained by methods described previously.²¹

Reactions in organic solvents (see Table I) involved mixing $\sim 0.5 M$ solutions at room temperature; the resultant precipitate was recrystallized from the reaction solvent unless otherwise noted. Indium chloride and bromide were prepared by dissolving the metal (Fisher Scientific Co.) in concentrated acid; the hydrated material obtained by evaporating this mixture to dryness was dissolved in the organic solvent. Indium(III) iodide was prepared by heating stoichiometric amounts of the elements *in vacuo*. Organic halide salts were used as received.

Melting points given are uncorrected. In some cases of

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melting with decomposition, free amine could be detected by smell.

In a number of reactions, the desired products were not obtained. Both $(\text{C}_2\text{H}_5)_3\text{NHCl}$ and $(\text{C}_2\text{H}_5)_3\text{NHBr}$ gave precipitates only after partial evaporation of ethanol; the precipitate contained no indium. With LiCl, NaCl, LiBr, and NaBr in a variety of concentrations of aqueous hydrohalic acid, we obtained either no precipitate or the original halide slightly contaminated with indium (usually $\sim 0.5\%$). Mixtures of substituted ammonium bromide, indium bromide, and excess urea in 4 or 6 M aqueous hydrobromic acid generally gave the CInBr_4 , C_2InBr_5 , or C_4InBr_7 compounds. With $\text{CH}_3\text{NH}_2\text{Br}$ in 6 M hydrobromic acid, the product contained 8.0% In and 69.3% Br; from 4 M aqueous HBr, the values were 12.9% In and 67.5% Br. With $(\text{CH}_3)_2\text{NH}_2\text{Br}$ in 4 M aqueous HBr, analysis of the solid gave 14.2% In and 63.6% Br. None of these analyses correspond to the $\text{InBr}_4\text{L}_2^-$ salts. No precipitate was obtained from an ethanolic solution of InI_3 and $\text{LiI} \cdot \text{H}_2\text{O}$.

Results and Discussion

Preparative Results.—We have obtained all of the chloride and bromide compounds reported by Ekeley and Potratz,⁶ together with the corresponding iodo complexes $(\text{C}_6\text{H}_5)_4\text{AsInI}_4$, $(\text{C}_6\text{H}_5)_3\text{CH}_3\text{AsInI}_4$, $(n\text{-C}_4\text{H}_9)_4\text{NInI}_4$, $(n\text{-C}_3\text{H}_7)_4\text{NInI}_4$, $(\text{CH}_3)_4\text{NInI}_4$, and CsInI_4 , not prepared by these authors. A number of new salts of indium(III)-bromo complexes were also obtained, including $(\text{CH}_3)_4\text{NInBr}_4$, $(n\text{-C}_4\text{H}_9)_4\text{NInBr}_4$, and $n\text{-C}_4\text{H}_9\text{-}(\text{C}_6\text{H}_5)_3\text{PInBr}_4$, along with two compounds of stoichiometry $((\text{CH}_3)_2\text{NH})_2\text{InBr}_7$ and $((\text{CH}_3)_3\text{NH})_3\text{InBr}_7$. Similar reactions with substituted ammonium chlorides gave, in addition to the compounds $((\text{CH}_3)_4\text{N})_2\text{InCl}_5$, $((\text{C}_2\text{H}_5)_4\text{N})_2\text{InCl}_5$, $((\text{CH}_3)_3\text{NH})_3\text{InCl}_6$, $((\text{CH}_3)_2\text{NH}_2)_2\text{InCl}_7$, and $(\text{CH}_3\text{NH}_2)_4\text{InCl}_7$ reported earlier,⁶ the new species $(\text{C}_2\text{H}_5)_4\text{NInCl}_4$, $(\text{C}_6\text{H}_5)_4\text{AsInCl}_4$, $(n\text{-C}_3\text{H}_7)_4\text{NInCl}_4$, $(\text{C}_6\text{H}_5\text{CH}_2(\text{C}_6\text{H}_5)_3\text{P})_2\text{InCl}_5$, and $((\text{CH}_3)_3\text{C}_6\text{H}_5\text{N})_2\text{InCl}_5$. There are therefore more than 25 known salts of organic cations and anionic indium(III) halide complexes, including two compounds which were first pre-

TABLE II
 THE VIBRATIONAL SPECTRA OF C[InX₄] SALTS (IN CM⁻¹)^a

	$\nu_1(a_1)$ R	$\nu_2(f_2)$		$\nu_3(f_2)$		Lattice mode Ir
		Ir	R	Ir	R	
(C ₂ H ₅) ₄ N[InCl ₄]	325 w	330 vs	333 vw	120 s 128 sh	116 vw	58 w
(<i>n</i> -C ₃ H ₇) ₄ N[InCl ₄]	326 m	333 vs ~340 sh	336 sh	115 s	110 vw	55 vw
(C ₆ H ₅) ₄ As[InCl ₄]	326 m	353 sh 346 s 331 sh	343 w	
InCl ₄ ⁻¹¹	321		337		112	
(C ₂ H ₅) ₄ N[InBr ₄]	199 s	237 s 232 sh	235 wm	88 m	...	53 vw
(<i>n</i> -C ₃ H ₇) ₄ N[InBr ₄]	200 s	241 m 233 s	238 wm	82 m	...	50 w
InBr ₄ ⁻¹¹	197		239		79	
(<i>n</i> -C ₃ H ₇) ₄ N[InI ₄]	139 s	188 s	186 w	62 wm	...	
InI ₄ ⁻¹¹	139		185		58	

^a $\nu_2(e)$ was not observed for any of these compounds.

pared by Renz²² and which can now be formulated as (pyH)₃InCl₆ and (quinH)₄InCl₇ (py = pyridine, quin = quinoline).

There are a number of references in the older literature to salts with inorganic cations (*vide supra*), but the only unsubstituted anionic indium(III) halide complex of this type which we have been able to obtain is CsInI₄. All attempts to prepare the various reported anhydrous MInCl₄ and M₃InCl₆ (M = Na, Rb, Cs, or NH₄) salts by crystallization from aqueous solution gave either compounds containing essentially no indium or material apparently containing excess MX (see Experimental Section). Complete evaporation of solutions gave solids which contained indium, but this technique does not yield crystalline materials. Furthermore, the relationship between the composition of such solids and the species obtained by crystallization or precipitation is at best tenuous, and these materials were therefore judged unsuitable for structural study.

Despite a series of reactions with cations of different size, with varying donor ligands, and under varying solution conditions, we were unable to obtain any crystalline monosubstituted species InX₅L²⁻, other than the monohydrates Cs₂[InCl₅(H₂O)], (NH₄)₂[InCl₅(H₂O)], ((CH₃)₄N)₂[InCl₅(H₂O)], and (NH₄)₂[InBr₅(H₂O)]. With the exception of the tetramethylammonium-chloro complex, all of these species have been described previously, as have the corresponding rubidium salts.^{3,4,17} The failure to obtain InX₅L²⁻ salts may be due to the use of inappropriate cations; on the other hand, it should be noted that there is no evidence for such complexes, other than the aquo species, in solution. For example, we found no change in the far-infrared spectrum of InCl₆²⁻ in dichloromethane on adding excess acetonitrile, implying either that the infrared spectra of InCl₅²⁻ and InCl₅(CH₃CN)²⁻ are accidentally coincident or that acetonitrile does not coordinate with In(III) under these conditions. Similar conclusions have been reached by Shriver and Wharf.¹⁵

Vibrational Spectra.—For the CInX₄ species, we find spectra in good agreement with those previously reported for solutions of the InX₄⁻ anions (see Table II), and all these species can therefore be formulated unambiguously as C⁺[InX₄]⁻ salts. In no case was the $\nu_2(e)$ vibration observed in the Raman spectra, since it was not possible to detect lines sufficiently close to the

exciting line with the equipment available. In most cases, $\nu_3(f_2)$ was found to be split in the infrared spectra.

For crystalline ((C₂H₅)₄N)₂[InCl₅], which has been shown to contain a square-pyramidal anion,⁸ our results are in good agreement with those of Shriver and Wharf.¹⁵ Infrared absorptions at 294 (s), 282 (s), 268 (s), 152 (sh), and 142 cm⁻¹, lattice modes at 59 (vw) and 45 cm⁻¹ (vw), and Raman lines at 294 (s), 287 (sh), 194 (w), 167 (m), 123 (m), and 106 cm⁻¹ (m) are consistent with C_{4v} symmetry for the anion (see also ref 16). We also recorded the spectra of ((CH₃)₄N)₂[InCl₅], (CH₃N(C₆H₅)₃)₂[InCl₅], and (C₆H₅CH₂(C₆H₅)₃-P)₂[InCl₅], but unfortunately the presence of several cation bands complicates the analysis, and in addition ((CH₃)₄N)₂[InCl₅] and (CH₃(C₆H₅)₃N)₂[InCl₅] gave rather poor Raman spectra. We find 295 (s) and 267 cm⁻¹ (s) (ir) and 295 cm⁻¹ (s) (R) for (CH₃(C₆H₅)₃-N)₂[InCl₅] and 296 (s), 278 (s), and 264 cm⁻¹ (s) (ir) and 294 (s) and 196 cm⁻¹ (w) (R) for (C₆H₅CH₂(C₆H₅)₃-P)₂[InCl₅]; ((CH₃)₄N)₂[InCl₅] gave 265 cm⁻¹ (s, br) (ir) and 288 (m) and 265 cm⁻¹ (w) (R). These limited results are consistent as far as they go with the presence of InCl₅²⁻ anions of the same C_{4v} symmetry as in ((C₂H₅)₄N)₂[InCl₅].

For the salt ((CH₃)₄N)₂InBr₅, vibrations are identified at 234 (wm), 200 (vs), 180 (wm), 78 (m), and 59 cm⁻¹ (w) in the Raman spectrum and 241 (sh), 230 (s), 204 (m), 102 (m), 83 (w), and 56 cm⁻¹ (vw) in the infrared spectrum. This is best interpreted as arising from a lattice of 2(C₂H₅)₄N⁺ + InBr₄⁻ + Br⁻, with the InBr₄⁻ anion in some site symmetry lower than T_d; the rather high ν (In-Br) modes are also consistent with this model. The structure proposed is in some ways analogous to that discussed below for the C₄InX₇ compounds. It is worth noting that while the reaction of (CH₃)₄NBr and InBr₃ in methanol or ethanol produces ((CH₃)₄N)₂InBr₅, the crystallization of a solution of these components in aqueous (4 M) hydrobromic acid yields (CH₃)₄N[InBr₄]. In some respects, this is similar to the (C₂H₅)₄N-In-Cl system, in that the composition of the crystal is dependent on the solution-phase conditions.⁸

If the salt ((CH₃)₃NH)₃InCl₆ contains the InCl₆³⁻ anion, the ir spectrum should show only two absorption bands, whereas in fact three are observed (Table III). Two of these (245 and 150 cm⁻¹) and the single Raman line (268 cm⁻¹) are in good agreement with previous results¹⁸ for InCl₆³⁻. It is worth noting here

TABLE III
THE VIBRATIONAL SPECTRA OF SOME CRYSTALLINE
INDIUM(III) HALIDE COMPLEXES (IN cm^{-1})

	R	Ir
$((\text{CH}_3)_3\text{NH})_3[\text{InCl}_6]$	268	245 vs, vbr, 182 vs, vbr, 150 s
$((\text{CH}_3)_2\text{NH}_2)_4\text{InCl}_7$	270	290 sh, 250 vs, 214 sh, 170 sh, 151 vs
$(\text{CH}_3\text{NH}_2)_4\text{InCl}_7$	278	262 vs, 216 sh, $\sim 182^a$, $\sim 164^a$
$(\text{CH}_3\text{NH}_2)_4\text{InBr}_7$	172	179 vs, vbr, 146 m, 106 w
$((\text{CH}_3)_2\text{NH}_2)_3\text{InBr}_7$	169	274 w, br, 186 vs, 170 vs, 142 w, 112 m, br

^a Not clearly resolved.

that the results for InCl_4^- , InCl_6^{2-} , and InCl_6^{3-} show a smooth decrease in the $\nu(\text{In-Cl})$ frequency as the coordination number increases from 4 (ν_1 325 cm^{-1}) to 6 (268 cm^{-1}).

The highest $\nu(\text{In-Cl})$ absorption in both C_4InCl_7 species is at $\sim 270 \text{ cm}^{-1}$ (Table III), close to that for InCl_6^{3-} , suggesting that this anion is the indium(III) species present in these compounds. The lattice is believed to contain four cations, an InX_6^{3-} anion, and a halide ion. Such species are known for other salts; an example involving a neighboring element is $(\text{NH}_4)_3\text{-SiF}_7$, studied by Hoard and Williams.^{23,24} The vibrational spectrum of $(\text{CH}_3\text{NH}_2)_4\text{InCl}_7$ is then that of InCl_6^{3-} , plus a broad lattice mode at approximately 170 cm^{-1} , which combines with ν_4 to give a very broad absorption band. The appearance of three bands at 290, 250, and 214 cm^{-1} is very similar to the splitting of ν_3 in the pseudooctahedral crystalline InCl_3 (290, 235, and 210 cm^{-1}) reported by Greenwood, Prince, and Straughan.²⁰ There are some differences in the ir spectrum of $((\text{CH}_3)_2\text{NH}_2)_4\text{InCl}_7$, notably in the presence of a doublet at 262 and 216 cm^{-1} in place of the triplet discussed above and in the higher energy region of the badly resolved low-frequency bands. The spectra of $(\text{CH}_3\text{NH}_2)_4\text{InBr}_7$ and $(\text{CH}_3\text{NH}_2)_3\text{InBr}_7$ can be understood on a similar basis, with the $\sim 170\text{-cm}^{-1}$ Raman-active band assigned to ν_1 of InBr_6^{3-} . No other species

(23) J. L. Hoard and M. B. Williams, *J. Amer. Chem. Soc.*, **64**, 633 (1942).

(24) A. F. Wells, "Structural Inorganic Chemistry," 3rd ed, Oxford University Press, London, 1962, p 684.

containing this anion were obtained in our preparative studies. The breadth of the ν_3 absorption at 179 cm^{-1} in $(\text{CH}_3\text{NH}_2)_4\text{InBr}_7$ and the series of bands in $((\text{CH}_3)_2\text{NH}_2)_4\text{InBr}_7$ are similar to those found for the corresponding chlorides and to the splitting noted in the spectrum of InBr_3 .²⁰ It is believed that in all cases this broadening is a consequence of a low site symmetry in the anion.

Relative Stabilities of Anionic Indium Complexes.—

The preparative and spectroscopic work, together with X-ray structure investigations,^{7,8} shows that differences in reaction conditions, such as change of solvent or change of cation, result in the precipitation of different solid phases from given reactants. We conclude that for these anionic species, as for other indium(III) complexes, the energy balance of those factors involved in stabilizing the species in solution and in the solid state is a delicate one.

Two general statements can be made about the stoichiometries of the species obtained in this work. *First*, for a given cation, or for cations of similar size, the coordination number of indium(III) decreases with increasing halogen size. A similar general conclusion applies to cationic indium(III) complexes²¹ and to the neutral adducts of the indium(III) halides,²⁵ and possible reasons for this effect have been discussed earlier.²¹ The *second* generality is that, for a given halide ligand, the coordination number of indium(III) decreases with increasing cation size. This is presumably a solid-state effect in the main, since the nature of the cation should have only a small influence on equilibria in non-aqueous solution. It is hoped to investigate these matters further in subsequent experiments.

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(25) A. J. Carty and D. G. Tuck, *J. Chem. Soc.*, 1081 (1966).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY OF TEXAS, AUSTIN, TEXAS 78712

Exchange Reactions of Borazines with Heavy Metal Halides

By G. A. ANDERSON AND J. J. LAGOWSKI*

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N-Trimethylborazine reacts with metal halides to yield partially halogenated derivatives of *N*-trimethylborazine as well as other reaction products: titanium tetrachloride and titanium tetrafluoride yield hydrogen and titanium trihalides; mercuric and mercurous chlorides yield hydrogen chloride and/or hydrogen and mercury; stannic chloride and stannic bromide yield hydrogen halides, hydrogen, and stannous halides; and stannic iodide does not react. Under the same conditions, stannic chloride does not react with hexamethylborazine nor does tetramethyltin react with *N*-trimethyl-*B*-trichloroborazine. Trans halogenation of *N*-trimethyl-*B*-dichloroborazine can be effected with titanium tetrafluoride.

Introduction

A number of reactions have been reported for borazines in which substitution occurs at the boron positions.¹ While the reagents in these reactions have

(1) H. I. Schlesinger, L. Horvitz, and A. B. Burg, *J. Amer. Chem. Soc.*, **58**, 409 (1936); H. I. Schlesinger, D. M. Ritter, and A. B. Burg, *ibid.*, **60**, 1296 (1938); G. W. Schaeffer, R. Schaeffer, and H. I. Schlesinger, *ibid.*, **73**, 1612 (1951); G. E. Ryschkewitsch, J. J. Harris, and H. H. Sisler, *ibid.*, **80**, 4515 (1958); R. I. Wagner and J. L. Bradford, *Inorg. Chem.*, **1**, 99 (1962); H. C. Newson, W. G. Woods, and A. L. McCloskey, *ibid.*, **2**, 36 (1963).

been predominantly other boron-containing compounds, the trans halogenation of *B*-trichloroborazines with titanium tetrafluoride² suggests that an exchange reaction using heavy metal halides as halogen sources is also possible. Indeed, preliminary results from this laboratory³ on *N*-trimethylborazine as well as similar

(2) K. Neidenzu, *ibid.*, **1**, 943 (1962).

(3) G. A. Anderson and J. J. Lagowski, *Chem. Commun.*, 649 (1966).