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Formation and Characterization of the Indium Hydride Molecules H_2InCl and $HInCl_2$: Matrix Isolation and Quantum Chemical Studies

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Abstract: Indium monochloride, InCl, adds HCl or H_2 when isolated together with these molecules in an argon matrix at 12 K and photoactivated by broad-band UV−visible radiation. On the basis of the infrared spectra of the matrices (including the effects of $^1H/^2H$ and $^{35}Cl/^{37}Cl$ isotopic change) and of density functional theory (DFT) calculations, the products of the reactions were identified as the discrete indium hydride molecules $HInCl_2$ and H_2InCl. $HInCl_2$ is also one of the products of the reactions brought about by photolysis of matrices containing In atoms and HCl; both $HGaCl_2$ and H_2GaCl are formed from Ga atoms under similar conditions. All six vibrational fundamentals ($3a_1 + 1b_1 + 2b_2$) of H_2InCl and five of the six vibrational fundamentals of $HInCl_2$ have been identified; normal coordinate and DFT calculations provide a framework for evaluating the physical properties of the two molecules.

Introduction

There is no little interest in volatile compounds of the group 13 metals with the potential to act as precursors in chemical vapor deposition (CVD) to the metals themselves or to compound semiconductors.[1,2] The most suitable compounds for this purpose should include bonds that are easily and quantitatively cleaved on the surface of the substrate to leave a clean metal or semiconductor film. In this context the hydride ligand has much to commend it:[3] it engages normally in only weak intermolecular interactions (thereby favoring volatility); it forms comparatively weak bonds to the group 13 metals (to give thermally labile compounds); decomposition of the metal hydride yields a highly volatile, comparatively inert product in H_2; and there is little opportunity for the formation of intermediate decomposition products (cf. the decomposition of organometallic species). Indeed, selected alane and gallane derivatives, such as $Me_3N{\cdot}AlH_3$, have been successfully used to deposit the metal from the gas phase for the growth, for example, of GaAlAs and metal-containing heterostructures or for the metallization of semiconductor devices.[3,4]

Although volatile hydride derivatives of aluminum and gallium are now well established,[2,3,5,6] the weakness of In−H bonds has generally thwarted attempts to prepare comparable indium derivatives. On the evidence of recent ab initio MP2 studies,[7] In_2H_6 appears to be highly unstable in both the gas and solid states, although modest kinetic stability in the gas phase may give just a glimmer of hope. Stabilization may be achieved by complexation,[3] as evidenced by the successful isolation of the adducts $Pr^{i}\overline{NC_2Me_2(Pr^{i})NC}{:}InH_3$[8] and $(cyclohexyl)_3P{\cdot}InH_3$,[9] but as yet volatilization of any such compound has been forestalled by its decomposition. Partial replacement of hydrogen in the parent hydride by other ligands with appropriate electronic and/or steric properties offers an alternative strategy for improving the thermal stability of the system. For example, introduction of a more electronegative ligand like chlorine may be expected to strengthen the remaining In−H bonds and produce relatively more robust compounds of the types $[H_2InCl]_n$ and $[HInCl_2]_n$. The known stabilities of the analogous gallium compounds[2,5] support this view, and a very recent report[10] indicates not only that $HInCl_2$ can be synthesized in solution but also that it is relatively long-lived in tetrahydrofuran solution at ambient temperatures and can be used in this form to reduce organic carbonyl and halogen compounds.

Matrix isolation has proved to be highly effective as a method of reconnaissance and characterization for previously unknown hydride derivatives of the group 13 metals.[11−13] For example, the simple InH_2 and InH_3 molecules have been formed by the reactions between indium and dihydrogen molecules or hydrogen atoms and identified for the first time in this way.[14] Photoexcitation of the In atoms is needed to promote insertion not only into the H−H bond of dihydrogen to give InH_2[14] but

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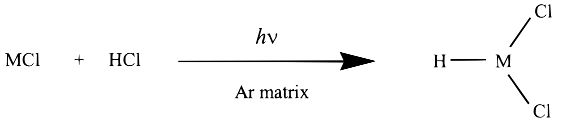
also into a C−H bond of methane to give CH_3InH.[15] The monochloride molecules MCl (M = Al or Ga) have emerged elsewhere as key synthons in matrix and solution media.[12] Thus, the simple mononuclear molecules $HMCl_2$ (M = Al[16] or Ga[17]) have been prepared by the photoactivated matrix reaction between MCl and HCl molecules (eq 1), and H_2GaCl is likewise produced by the reaction between GaCl and H_2 (eq 2).[18]



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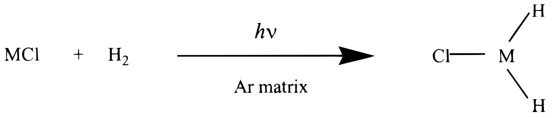

(2)

We have been using matrix isolation to extend the known chemistry of group 13 metal atoms M, their dimers M_2, and other derivatives.[19] Here we report on the outcome of the photolytically induced reactions of matrix-isolated InCl molecules with HCl and H_2. The course of events has been tracked through the infrared spectra of the matrices, and the identities of the products have been confirmed (i) by the response to deuteration and to the natural presence of the two chlorine isotopes ^{35}Cl and ^{37}Cl, (ii) by comparison with the results of density functional theory (DFT) calculations, (iii) by normal coordinate analysis, and (iv) by reference to the properties of related molecules.

Experimental Section

Indium monochloride, InCl (used as supplied by Aldrich, stated purity 99.999%), was vaporized from a tantalum Knudsen cell which was heated resistively to ∼550 °C. Gallium (Aldrich, 99.9999% pure) and indium (Aldrich, 99.999% pure) were each evaporated similarly but at a temperature of ∼950 °C. Hence the vapor was co-deposited with an excess of HCl- or H_2-doped argon on a CsI window cooled normally to 12 K by means of a Displex closed-cycle refrigerator (Air Products, model CS202). The estimated proportions InCl:Ar were in the order of 1:100, and Ga/In:Ar in the order of 1:600.

H_2 (BOC, research grade), D_2 (Aldrich, 99.98 at %), HD (Aldrich, 96% HD, 4% H_2 and D_2), and argon (BOC, Research grade) were used as supplied. HCl (Aldrich, stated purity >99%) was purified by fractional condensation in vacuo prior to use. DCl was synthesized by the reaction between PCl_3 and D_2O (both from Aldrich) and also purified by similar means. Gas mixtures of argon with HCl (or DCl) or H_2 (or D_2) were prepared by standard manometric methods, the concentration of the active ingredient being normally ∼5%. Typical deposition rates were ∼2 mmol of matrix gas per hour, continued over a period of 2−3 h.

Following deposition and infrared analysis of the resulting matrix, the sample was exposed to broad-band UV−visible radiation from a Spectral Energy Hg−Xe arc lamp operating at 800 W. The output from the lamp was normally limited only by a water filter to absorb infrared radiation and so minimize any heating effects. Infrared spectra of the matrix samples were recorded at a resolution of 0.5 cm^{-1} and with an accuracy of ±0.1 cm^{-1} using a Nicolet Magna-IR 560 FTIR instrument equipped either with an MCTB or with a DTGS detector (for the ranges 4000−400 cm^{-1} or 600−200 cm^{-1}, respectively).

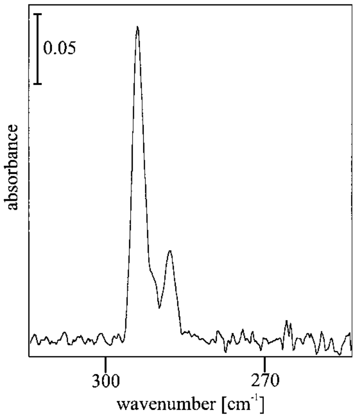

Figure 1. Infrared spectrum of InCl isolated in a pure Ar matrix.

Density functional theory (DFT) calculations were performed using the GAUSSIAN98 program package[20] and applying the B3LYP-method which has been shown to give satisfactory results for small group 13 metal compounds.[21] A LANL2DZ basis set was employed for all elements (In, Cl, and H) in InCl, $HInCl_2$, and H_2InCl. Normal coordinate calculations depended on the program ASYM 40.[22]

Results

(a) InCl. Figure 1 illustrates the infrared spectrum of the matrix formed by co-condensing InCl vapor with an excess of pure argon at ∼12 K. The spectrum contains but a single absorption split into a doublet with maxima at 293.9 and 287.8 cm^{-1}. The relative intensities of the two components (∼3.3:1) and the frequency difference (6.1 cm^{-1}) make it clear that they arise from the isotopomers $In^{35}Cl$ and $In^{37}Cl$, respectively (isotopic shift calculated for a harmonic InCl oscillator 6.15 cm^{-1}). The results tally well with those given in an earlier report of the matrix-isolated InCl molecule as formed by the reaction of the metal atoms with Cl_2.[23] The gaseous molecule has been characterized quite fully, notably by its electronic spectrum.[24] The corresponding (anharmonic) frequency for gaseous InCl is 315.6 cm^{-1},[24] implying a relatively large red shift of 21.7 cm^{-1} (i.e., 6.8%) when the molecule is isolated in an Ar matrix. AlCl and GaCl show comparable red shifts in similar circumstances, namely, AlCl 22.4 cm^{-1} (4.7%)[25] and GaCl 20.0 cm^{-1} (5.5%),[17] in keeping with the polarity of these heteronuclear diatomic molecules.[26]

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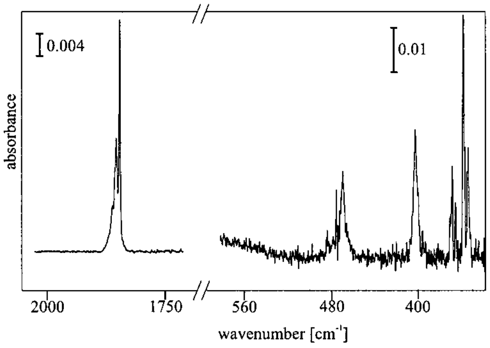

Figure 2. Infrared spectrum of an Ar matrix formed by co-deposition of InCl vapor with HCl following photolysis with broad-band UV−visible light ($\lambda = 200-800$ nm) for 1 h.

It seems likely that aggregates of InCl are also trapped in the matrix, although the vapor is reported to contain only a low concentration of such aggregates under conditions comparable with those of the present experiments. On the evidence of species such as $[AlCl]_2$[16] and $[GaCl]_2$,[17,18] however, the ν(In−Cl) frequencies of these may be expected to occur at frequencies close to, or below, the lower threshold (200 cm^{-1}) of our measurements.

(b) InCl + HCl. On deposition, an argon matrix containing InCl and HCl exhibited, in addition to the infrared absorptions due to InCl, HCl, and its aggregates $[HCl]_n$,[27] a new feature centered at 265.9/258.8 cm^{-1}. The obvious explanation of this extra band is that it corresponds to ν(In−Cl) of a loosely bound complex InCl···HCl. There was no other clear sign of reaction between InCl and HCl under these conditions, the only remaining weak bands all being identifiable with H_2O,[28] CO_2[29] and other trace impurities.

Exposure of the matrix to broad-band UV−visible radiation ($200 < \lambda < 800$ nm) for 1 h resulted in significant changes, as revealed by the infrared spectrum measured at this stage (see Figure 2). The band due to InCl had decreased in intensity and that at 265.9/258.8 cm^{-1} had disappeared, to be replaced by new features at 1846.9, 469.7, 402.6, 369.1/365.9, and 358.5/354.2 cm^{-1}. The new high-frequency bands occur in the region where In−H stretching modes might be expected, although the frequencies are appreciably higher than those reported previously for the matrix-isolated molecules InH (1438.6 cm^{-1}), InH_2 (1615.6 and 1548.6 cm^{-1}), and InH_3 (1754.5 cm^{-1}).[14] The doublet patterns and intervals of the bands between 300 and 400 cm^{-1}, each with a high-frequency component more intense than the low-frequency one, bear all the hallmarks of ν(In−Cl) modes of one or more products.

A similar experiment was carried out but with DCl in place of HCl. Following deposition, the matrix showed only one absorption that could not be attributed to DCl, $[DCl]_n$, InCl, or traces of impurities, and this appeared at 265.3/258.2 cm^{-1}, only marginally shifted with respect to the corresponding signal observed in the HCl experiment. Broad-band UV−visible irradiation for 1 h then resulted in the virtual extinction of this band as well as partial decay of the InCl band. At the same time significant changes of position were observed for some of the new bands: that at 1846.9 cm^{-1} shifted to 1325.6 cm^{-1} (H/D = 1.3735:1). Large shifts were also observed for the bands at 469.7 and 402.6 cm^{-1}, the counterparts to which occurred at 311.2 and 304.8 cm^{-1} with H/D = 1.5093:1 and 1.3209:1, respectively. On the other hand, the remaining low-frequency bands suffered shifts amounting at most to 30 cm^{-1} (see Table 1).

Table 1. Infrared Absorptions for the Reaction of InCl with HCl/DCl (Frequencies in cm^{-1})

InCl + HCl	InCl + DCl	deposition[a]	broadband photolysis[a]	absorber[b]
1846.9	1325.6	-	↑	$HInCl_2$
469.7	311.2	-	↑	$HInCl_2$
402.6	304.8	-	↑	$HInCl_2$
369.1/365.9	368.8/363.8	-	↑	$HInCl_2$
358.5/354.2	385.1/383.0	-	↑	$HInCl_2$
292.8/286.6	292.8/286.6	↑	↓	InCl
265.9/258.8	265.3/258.2	↑	↓	InCl···HCl

[a] ↑: increase in intensity. ↓: decrease in intensity. [b] Identified only for the HCl product.

(c) InCl + H_2. The infrared spectrum of the matrix formed by co-condensing InCl vapor with an excess of H_2-doped argon was not perceptibly different from that of InCl trapped in an undoped argon matrix. There was no sign of an additional absorption analogous to that near 265 cm^{-1} in the experiments with HCl and suggestive of complexation between the H_2 and InCl molecules. Similar experiments have recently signaled specific and quite strong interaction between H_2 and CuCl, notably through the appearance of a new infrared band at 3222 cm^{-1} attributable to the ν(H−H) mode of what is presumed to be an η^2-H_2 unit.[30] Quantum chemical studies give grounds also for believing that Al^+ binds H_2 weakly with an energy of about 4 kJ mol^{-1}, although this energy increases sharply as the cation charge increases.[31] However, in neither the high-frequency nor the low-frequency region of the infrared spectrum did the matrix combination of InCl and H_2 give any hint of such complexation.

On the other hand, irradiation of the matrix with broad-band UV−visible light for 1 h led to the appearance of 11 new infrared features located at 3649.3, 1857.2, 1820.3, 1804.0, 810.0, 606.4, 575.8, 541.4, 451.6, 415.7, and 343.4 cm^{-1} at the expense of a partial decay of the InCl doublet at ~290 cm^{-1} (see Table 2 and Figure 3). The corresponding spectra of a matrix containing InCl and D_2 likewise gave no sign of any reaction prior to broad-band UV−visible photolysis. Thereafter, the spectrum again witnessed the growth of 11 new bands, mostly shifted to significantly lower wavenumbers with respect to their counterparts in the experiments with H_2. Thus, the signals at 1820.3 and 1804.0 cm^{-1} were replaced by ones at 1310.9 and 1291.9 cm^{-1}, corresponding to H/D ratios of 1.3886:1 and 1.3964:1, respectively. Similarly at lower frequencies the bands at 575.8, 541.4, and 415.7 cm^{-1} in the earlier experiments correlated with those at 415.2, 389.1, and 298.2 cm^{-1} in the D_2 experiment, giving H/D ratios of 1.3865:1, 1.3914:1, and 1.3940:1. It was evident therefore that all of the relevant vibrations involve primarily motion of one or more hydrogen atoms. Only the doublet at lowest frequency, that is, 343.4/336.2 cm^{-1}, showed but a small shift (to 339.3/333.0 cm^{-1}) on deuteration of the carrier. The five signals at 3649.3, 1857.2, 810.0, 606.4, and 451.6 cm^{-1} gave no sign of any shift. Varying the conditions of the experiment shows that the six

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Table 2. Infrared Absorptions for the Reaction of InCl with $H_2/D_2/HD$ (Frequencies in cm^{-1})

$InCl + H_2$	$InCl + D_2$	$InCl + HD$	dep.[a]	broadband photolysis[a]	absorber[b]
3649.3	3649.3	3649.3	-	↑	HInCl(OH)
1857.2	1857.2	1857.2	-	↑	HInCl(OH)
1820.3	1310.9	1811.1	-	↑	H_2InCl
1804.0	1291.9	1301.0	-	↑	H_2InCl
810.0	810.0	810.0	-	↑	HInCl(OH)
606.4	606.4	606.4	-	↑	HInCl(OH)
575.8	415.3	523.4	-	↑	H_2InCl
541.4	389.1	475.0	-	↑	H_2InCl
451.6	451.6	451.6	-	↑	HInCl(OH)
415.7	298.2	326.9	-	↑	H_2InCl
343.4/336.2	339.3/333.0	348.6/342.2	-	↑	H_2InCl
293.9/287.8	293.9/287.8	293.9/287.8	↑	↓	InCl

[a] ↑: increase in intensity. ↓: decrease in intensity. [b] Identified only for the H_2 product.

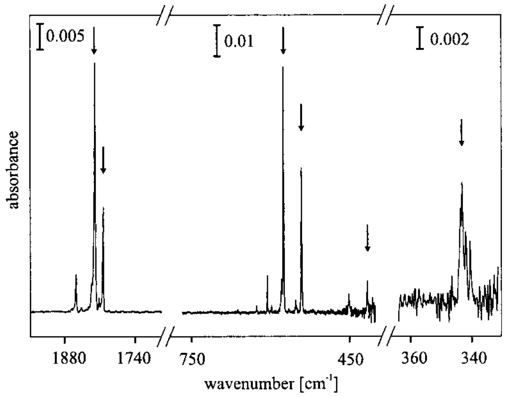

Figure 3. Infrared spectrum of an Ar matrix formed by co-deposition of InCl vapor with H_2 following photolysis with broad-band UV−visible light ($\lambda = 200-800$ nm) for 1 h. The arrows mark bands due to H_2-InCl.

features at 1820.3, 1804.0, 575.8, 451.4, 415.7, and 343.4 cm^{-1} all belong to a common absorber, whereas the five weaker bands at 3649.3, 1857.2, 810.0, 606.4, and 451.6 cm^{-1} belong to a different product arising from the reaction of InCl, not with HCl but with traces of H_2O.

Additional experiments were carried out using an HD-enriched mixture of H_2, D_2 and HD. In addition to the features observed in the experiments where pure H_2 and D_2 were used, new strong signals appeared at 1811.1, 1301.0, 523.4, 475.0, 348.6/342.2, and 326.9 cm^{-1}. These six additional bands were not observed when the experiment was performed with a 1:1 mixture of D_2 and H_2. It follows that the extra bands have their origin in the reaction of HD with InCl. Comparisons of frequency and intensity enabled the new bands to be correlated with those observed in the previous experiments, involving H_2 or D_2.

Discussion

The main infrared features observed to develop on co-depositing mixtures of InCl and either HCl or H_2 with an excess of argon before and after photolytic activation will be shown to arise from the molecules InCl, InCl···HCl, $HInCl_2$, and H_2-InCl. We now consider each of the molecules in turn.

(a) InCl. There can be no doubt about the identification of the doublet at 293.9/287.8 cm^{-1} with the ^{35}Cl and ^{37}Cl isotopomers of the diatomic molecule InCl, which has been similarly identified in earlier matrix studies.[23] The unusually large matrix shift of 6.8% from the gas-phase frequencies must be attributed to the solvating effect of the weakly polarizable cage of argon atoms surrounding the polar InCl molecule. It has been shown that the simple Onsager model of solvation is able adequately to reproduce the matrix shift experienced by a GaCl molecule.[26] DFT calculations give an optimum $^{115}In^{35}Cl$ molecule with $r_e(In-Cl) = 2.468$ Å and $\omega_e = 289.0$ cm^{-1}, in satisfactory agreement with the experimental values of 2.401 Å and 317.4 cm^{-1}, respectively.[24] On the assumption that the argon matrix can be treated as a homogeneous medium with a relative permittivity $\epsilon = 2$, the Onsager theory leads to a reduction in ω_e from 289.0 to 277.5 cm^{-1}, with an implied lengthening of the In−Cl bond from 2.468 to 2.491 Å. Hence the behavior of InCl, like that of GaCl,[26] can be interpreted adequately in this way.

In similar matrix studies of GaCl vapors, the presence of the dimer $[GaCl]_2$ was revealed by the appearance of infrared bands at 221 and 209 cm^{-1}.[17,18,26] Although studies of InCl vapors[32] suggest that $[InCl]_2$ is but a minor constituent at temperatures and pressures comparable with those operative in our experiments, the proportion of the dimer may well increase on co-condensation of the vapor with argon at ~12 K. Unfortunately, the low-frequency threshold of 200 cm^{-1} set by our infrared measurements ruled out the possibility of detecting $[InCl]_2$, but subsequent studies give no reason to believe that this molecule is a significant player in the reactions with HCl and H_2 brought about by photolysis.

An overview of the frequencies and force constants for monochloride molecules formed by metals of groups 1, 12, and 13 is given in Table 3a. Hence it emerges that InCl has a force constant close to that of HgCl, whereas in a given period the force constants decrease in the order group 12 > group 13 ≫ group 1, as the ionic characters of the molecules increase. In comparing the force constants k of analogous gallium(I) and indium(I) species (see Table 3b), it is clear (i) that $k(GaX) > k(InX)$, where X = OH, CH_3, Cl, or H, and (ii) that $k(MOH) \gg k(MCH_3) \geq k(MCl) > k(MH)$, where M = Ga or In. Changes of ionic character and orbital overlap are likely to be the main, frequently conflicting agents of these variations.

(b) InCl···HCl. The new infrared signal at 265.9/258.8 cm^{-1} observed immediately after deposition of InCl with HCl-doped argon must correspond to the $\nu(In-Cl)$ fundamental of the weakly bound adduct InCl···HCl. Under similar conditions both $AlCl$[16] and $GaCl$[17,26] give evidence of forming analogous species, each characterized by a $\nu(M-Cl)$ frequency (M = Al or Ga) significantly red-shifted with respect to that of the uncomplexed molecule. Expressed as a percentage, the frequency shift induced by this complexation varies from 5.5% for AlCl, through 11.5% for GaCl, to 9.5% for InCl. We fail to see any sign of the $\nu(H-Cl)$ mode of the InCl·HCl complex,

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Table 3. M−Cl Frequencies [cm^{-1}] and Force Constants [mdyn/Å]

(a) Groups 1, 12, and 13 Metal Halides

species	$\nu(M^{35}Cl)$	f	ref
AlCl	455.0	1.869	25
GaCl	342.9	1.628	33
InCl	293.9	1.379	24, 33
ZnCl	385	2.007	34
HgCl	287	1.461	34
LiCl	579	1.055	35
NaCl	335	0.927	35
KCl	248	0.663	36
RbCl	206	0.614	36

(b) Monovalent Ga and In Compounds

species	f(M = Ga)	f(M = In)	ref
M−H	1.342	1.133	14
M-Cl	1.628	1.379	24, 33
M-OH	3.027	2.385	37
M-CH$_3$	1.653	1.584	15

Table 4. Calculated Geometries for Relevant Molecules

species	molecule	symmetry	M−H [Å]	M−Cl [Å]	H−M−H [deg]
MH$_3$	AlH$_3$	D_{3h}	1.589	-	120.0
	GaH$_3$	D_{3h}	1.573	-	120.0
	InH$_3$	D_{3h}	1.780	-	120.0
H$_2$MCl	H$_2$AlCl	C_{2v}	1.588	2.211	127.3
	H$_2$GaCl	C_{2v}	1.566	2.224	129.7
	H$_2$InCl	C_{2v}	1.716	2.391	131.9
HMCl$_2$	HAlCl$_2$	C_{2v}	1.575	2.189	117.7
	HGaCl$_2$	C_{2v}	1.553	2.198	116.3
	HInCl$_2$	C_{2v}	1.702	2.361	114.6

Table 5. Observed and Calculated Infrared Frequencies (in cm^{-1}) for HInCl$_2$/DInCl$_2$

HIn^{35}Cl$_2$		DIn^{35}Cl$_2$			
obsd	calcd[a]	obsd	calcd[a]	assign't	description of vibrational mode
1846.9	1820.1 (72)	1325.6	1293.0 (39)	$\nu_1(a_1)$	ν(In−H)
369.1	328.8 (15)	368.8	328.5 (15)	$\nu_2(a_1)$	ν_{sym}(In−Cl)
[b]	102.1 (13)	[b]	102.0 (13)	$\nu_3(a_1)$	δ(InCl$_2$)
402.6	360.4 (75)	304.8	263.5 (45)	$\nu_4(b_1)$	γ
469.7	513.3 (137)	311.2	368.7 (34)	$\nu_5(b_2)$	ρ(H)
358.5	348.0 (61)	385.1	345.9 (95)	$\nu_6(b_2)$	ν_{asym}(In−Cl)

[a] C_{2v} geometry: r(In−H) 1.702 Å, r(In−Cl) 2.361 Å, Cl−In−Cl 114.6°. Intensities (km mol^{-1}) are given in parentheses. [b] Wavenumber too low for detection.

possibly because it is obscured by the bands of the different HCl aggregates which are present in the matrix in small but significant amounts.

As noted earlier, infrared measurements gave no sign to indicate the formation of a similar adduct when InCl was codeposited with H$_2$. However, studies by Andrews et al.[38] have demonstrated that argon may interact with a trapped acid or base molecule X at least as strongly as H$_2$, so that the solvating effect of an argon matrix is quite capable of obscuring the weak mutual perturbation of the components making up an X···H$_2$ contact pair.

(c) HInCl$_2$. On the evidence of the infrared spectrum, broadband UV−visible photolysis of a matrix containing InCl and HCl together results in the formation of a single product, primarily at the expense of the adduct InCl···HCl. The infrared spectrum of this product, allied to the circumstances of its formation and to comparisons with the behaviors of the AlCl/HCl[16] and GaCl/HCl[17] systems under similar conditions, gives good grounds for believing it to be the indium(III) compound HInCl$_2$. Such a molecule may be expected to be planar and thus possess C_{2v} symmetry under which the six vibrational fundamentals span the representation $3a_1 + 1b_1 + 2b_2$. The feature at highest frequency (1846.9 cm^{-1}) is then readily attributed to the In−H stretching vibration, $\nu_1(a_1)$. Analogies with the molecules HAlCl$_2$[16] and HGaCl$_2$[17] provide clear precedents for the assignment of the bands at 469.7 and 402.6 cm^{-1} to the in-plane In−H rocking fundamental, $\nu_5(b_2)$, and the out-of-plane In−H bending fundamental, $\nu_4(b_1)$, respectively. Strong support for these proposals comes from the large H/D shift displayed by each of the bands, the unusually large H/D ratio of 1.5093:1 associated with ν_5 being matched by a value of 1.4451:1 for the corresponding mode of HGaCl$_2$.[17] The frequencies, multiplet structures, and small H/D ratios give us strongly to believe that the two remaining bands correspond to the ν(In−Cl) fundamentals, the more intense doublet at 358.5/354.2 cm^{-1} being identified with the antisymmetric mode, $\nu_6(b_2)$ (H/D = 0.9309:1) and the less intense doublet at 369.1/365.9 cm^{-1} with the symmetric mode, ν_2 (a_1) (H/D = 1.0008:1). Under similar conditions the related HMCl$_2$ molecules are characterized by the following frequencies (in cm^{-1}) for the ν(M−Cl) modes, the relevant H/D ratios being given in parentheses: HAl^{35}Cl$_2$ ν_5 578.9 (0.9685:1), ν_2 481.3 (1.0080:1);[16] HGa^{35}Cl$_2$ ν_5 437.3 (0.9312:1), ν_2 414.3 (0.9995:1).[17] The only fundamental of HInCl$_2$ that has not been located is then the in-plane δ(InCl$_2$) mode, $\nu_3(a_1)$. The analogous mode of HGaCl$_2$ also escaped detection,[17] being expected to occur near 130 cm^{-1}. With an even lower frequency almost inevitable, ν_3 for HInCl$_2$ is almost certainly well below 200 cm^{-1}, the lower limit for spectroscopic detection in the present experiments. In summary, the observed spectrum is wholly consistent with the presence of the molecule HInCl$_2$ in the photolyzed matrix.

The Cl−In−Cl bond angle, θ, can be estimated roughly from the relative intensities in infrared absorption of the antisymmetric and symmetric ν(In−Cl) fundamentals, provided that these can be realistically factored out from the vibrational secular equation.[39] A ratio of I_{asym}/I_{sym} of 2.545:1 derived from the measured spectrum implies through eq 3 that θ is about 111°.

$$\frac{I_{asym}}{I_{sym}} = \left(\tan^2\frac{\theta}{2}\right)\frac{m_{In} + 2m_{Cl}\sin^2\frac{\theta}{2}}{m_{In} + 2m_{Cl}\cos^2\frac{\theta}{2}} \qquad (3)$$

We have also had recourse to DFT calculations to anticipate the optimum structures of the molecules HAlCl$_2$, HGaCl$_2$, and HInCl$_2$. The results, as listed in Table 4, are in satisfactory agreement with those computed previously for HGaCl$_2$[18,40] on the basis of ab initio MP2 and other methods. Hence it appears that the Cl−M−Cl angle θ decreases from the ideal value of 120° found in MH$_3$ and MCl$_3$ to 117.7, 116.3, and 114.6° in HMCl$_2$ for M = Al, Ga, and In, respectively. At 114.6° the theoretical estimate of θ for HInCl$_2$ compares well with the

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Table 6. Comparison of Infrared Absorptions of $HMCl_2/DMCl_2$ Compounds (M = Group 13 Element; Frequencies in cm^{-1})

assignment approx description		$\nu_1(a_1)$ ν(M−H)	$\nu_2(a_1)$ ν_{sym}(M−Cl)	$\nu_3(a_1)$ $\delta(MCl_2)$	$\nu_4(b_1)$ γ	$\nu_5(b_2)$ ν_{asym}(M−Cl)	$\nu_6(b_2)$ ρ(H)
$HBCl_2$[a]		2617	740	*d*	784	1089	*d*
$DBCl_2$[a]		1969	*d*	*d*	645	1005	*d*
$HAlCl_2$[b]		1967.6	481.3	*d*	471.8	578.9	654.5
$DAlCl_2$[b]		1430.1	477.5	*d*	355.4	597.7	*d*
$HGaCl_2$[c]		2015.3	414.3	*d*	464.3	607.5	437.3
$DGaCl_2$[c]		1450.2	414.5	*d*	*d*	420.4	469.6
$HInCl_2$	obsd	1846.9	369.1	*d*	402.6	469.7	358.5
	calcd	1820.1 (72)	328.8 (15)	102.1 (13)	360.4 (75)	513.3 (137)	348.0 (61)
$DInCl_2$	obsd	1325.6	368.8	*d*	304.8	311.2	385.1
	calcd	1293.0 (39)	328.5 (15)	102.0 (13)	263.5 (45)	345.9 (95)	368.7 (34)

[a] Reference 41. [b] Reference 16. [c] Reference 17. [d] Not observed.

Table 7. Measured and Calculated Infrared Frequencies (in cm^{-1}) for H_2InCl

$H_2In^{35}Cl$		$D_2In^{35}Cl$		$HDIn^{35}Cl$			
obsd	calcd[a]	obsd	calcd[a]	obsd	calcd[a]	assignment	description of vibrational mode
1804.0	1786.0 (42)	1291.9	1264.8 (22)	1301.0	1271.4	$\nu_1(a_1)$	ν_{sym}(In−H)
575.8	626.3 (240)	415.3	445.6 (119)	523.4	563.3	$\nu_2(a_1)$	$\delta(InH_2)$
343.4	325.0 (37)	339.3	324.9 (39)	348.5	324.8	$\nu_3(a_1)$	ν(In−Cl)
541.4	525.9 (165)	389.1	378.1 (88)	475.0	458.0	$\nu_4(b_1)$	γ
1820.3	1792.9 (191)	1310.9	1277.1 (100)	1811.1	1789.3	$\nu_5(b_2)$	ν_{asym}(In−H)
415.7	419.0 (51)	298.2	303.5 (29)	326.9	334.5	$\nu_6(b_2)$	ρ(Cl)

[a] C_{2v} geometry: *r*(In−Cl) 2.391 Å, *r*(In−H) 1.716 Å, H−In−H 131.9°. Intensities (km mol^{-1}) are given in parentheses.

order-of-magnitude value of 111° based on experiment. A harmonic force field calculated for the optimum geometry yields the vibrational frequencies and infrared intensities compiled alongside the experimental parameters in Table 5. The agreement between theory and experiment, with an rms deviation of 10.4% between observed and calculated frequencies, is reasonable and thus lends support to our interpretation of the matrix spectrum. Table 6 compares the IR absorptions observed for $HMCl_2$ compounds (M = B, Al, Ga, and In).

Of the anion $[ClHCl]^-$ [42] the infrared spectrum of the photolyzed matrix gave no hint. In this respect, too, InCl follows the precedents set by AlCl[16] and GaCl.[17] The response to deposition and photolysis of a group 13 metal chloride in the presence of HCl thus contrasts with that of an alkali-metal chloride which reacts spontaneously to form an ion-pair of the type $M^+[ClHCl]^-$.[42] Doubtless the difference reflects the superior basicity of the alkali-metal chloride molecule (cf. the weak interaction between InCl and HCl) and the remaining capacity for charge transfer from the M^I center when M is a group 13 metal.

(d) H_2InCl. An argon matrix containing InCl together with H_2 proves also to be susceptible to broad-band UV−visible photolysis, again giving a single product with an infrared spectrum now implying the presence of not one but two terminal In−H bonds and a single In−Cl bond. Hence, InCl appears once again to emulate GaCl under similar conditions (see eq 2),[18] and the new product is most likely to be the indium hydride H_2InCl, a conclusion amply supported by the effects of exchanging ^1H for ^2H and of having the two naturally occurring isotopes of chlorine, ^{35}Cl and ^{37}Cl. Like $HInCl_2$ and InH_3,[14] H_2InCl is almost certainly planar and thus possesses C_{2v} symmetry with a vibrational representation identical to that of $HInCl_2$. The measured infrared spectrum appears to give experimental access to all six of the vibrational fundamentals.

The two high-frequency absorptions at 1820.3 and 1804.0 cm^{-1} are clear candidates for the antisymmetric and symmetric In−H stretching modes, that is, $\nu_5(b_2)$ and $\nu_1(a_1)$, respectively. Although the frequencies are significantly lower than those of the corresponding modes in H_2GaCl,[18] the effects of deuteration reveal through the following H/D ratios obvious parallels between the two molecules: H_2GaCl, ν_1 1.3951:1, ν_5 1.3829:1; H_2InCl, ν_1 1.3964:1, ν_5 1.3886:1. The frequencies of the ν(In−H) modes are thus close to those of the corresponding modes reported not for H_2GaCl but for the radical H_2GeCl (1856 and 1810 cm^{-1}) also isolated in an argon matrix,[43] suggesting M−H bonds of comparable strength in these two molecules. The ratio of the intensities of the bands for H_2InCl, I_{asym}/I_{sym}, is found to be 3.250:1, and with due modification of eq 3, this implies an H−In−H bond angle in the order of 120°.

That the strong absorption at 575.8 cm^{-1} represents the InH_2 scissoring vibration, $\nu_2(a_1)$, is argued both by an H/D ratio of 1.3865:1 and by analogy with the corresponding feature of H_2GaCl (at 731.4 cm^{-1}, H/D = 1.3968:1).[18] Next in order of decreasing frequency is a band at 541.4 cm^{-1} for which the H/D ratio is 1.3914:1, and comparison with the spectrum of H_2GaCl (620.0 cm^{-1}, H/D = 1.3813:1)[18] leads us to assign this to the out-of-plane deformation mode, $\nu_4(b_1)$. Last to display a large H/D ratio (1.3940:1) is the feature at 415.7 cm^{-1} which is most plausibly identified with the in-plane rocking mode $\nu_6(b_2)$ (cf. H_2GaCl 510.1 cm^{-1}, H/D = 1.3740:1).[18] That leaves only the band at lowest frequency which shows only a small shift on deuteration (H/D = 1.0121:1) as well as evidence of the doublet pattern to be expected of what is substantially the ν(In−Cl) fundamental, $\nu_3(a_1)$. The frequencies for the mixed isotopomer HDInCl may then be assigned by comparison with those displayed by the two parent molecules. The corresponding frequencies are given in Table 7.

Table 4 includes details of the optimum geometries computed by DFT methods for molecules of the type H_2MCl (M = Al, Ga, or In). Where comparisons are possible, the dimensions thus calculated are in line with those derived from previous quantum chemical analyses.[18,40] Extension of our calculations to the

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Table 8. Comparison of the Infrared Absorptions Due to Different Isotopomers of H_2MCl (M = Ga or In; Frequencies in cm^{-1})

assignment approx description		$\nu_1(a_1)$ ν_{sym}(M−H)	$\nu_2(a_1)$ $\delta(MH_2)$	$\nu_3(a_1)$ ν(M−Cl)	$\nu_4(b_1)$ γ	$\nu_5(b_2)$ ν_{asym}(M−H)	$\nu_6(b_2)$ ρ(Cl)
H_2GaCl[a]	obsd	1964.6	731.4	406.9	620.0	1978.1	510.1
HDGaCl[a]	obsd	1971.9	661.0	409.8	544.3	1419.4	*b*
D_2GaCl[a]	obsd	1408.3	523.6	406.4	448.9	1430.5	371.2
H_2InCl	obsd	1804.0	575.8	343.4	541.4	1820.3	415.7
	calcd	1786.0 (42)	626.3 (240)	325.0 (37)	525.9 (165)	1792.9 (191)	419.0 (51)
HDInCl	obsd	1301.0	523.4	326.9	475.0	1811.1	348.6
	calcd	1271.4	563.3	324.8	458.0	1789.3	334.5
D_2InCl	obsd	1291.9	415.3	339.3	389.1	1310.9	298.2
	calcd	1264.8 (22)	445.6 (119)	324.9 (39)	378.1 (88)	1277.1 (100)	303.5 (29)

[a] Reference 18. [b] Not observed.

complete series of molecules MH_3, H_2MCl, $HMCl_2$, MCl_3 indicates that M−H bonds become shorter with progressive replacement of hydrogen by chlorine; the effect is small for M = Al or Ga, rather larger for M = In. Conversely, M−Cl bonds become longer with progressive replacement of chlorine by hydrogen. Oxidation of the monovalent species InH (r_e = 1.859 Å) and InCl (r_e = 2.468 Å) to the trivalent derivatives H_nInCl_{3-n} ($n = 0-3$) results in a marked shortening of the relevant bond distances. Whereas the Cl−M−Cl bond angle in $HMCl_2$ molecules is 2.3−5.4° less than 120°, the H−M−H bond angle in H_2MCl molecules is 7.3−11.9° *greater* than 120°, features qualitatively in keeping with the expectations of valence shell electron pair repulsion (VSEPR) Theory.[44] With a predicted H−In−H bond angle of 132°, H_2InCl also conforms to the pattern set by a wide range of H_2MX species, where the H−M−H angle is close to 130° and varies but little with the nature of X, irrespective of whether X takes the form of a mono- or bidentate unit (e.g., η^2-H_2MH_2, η^2-$H_2B_3H_6$, η^2-Cl_2GaH_2, etc.).[45]

A harmonic force field based on the optimum geometry deduced for H_2InCl yields the vibrational frequencies and infrared intensities listed in Table 7. The ability of the calculations to reproduce both the frequencies (with an rms deviation of no more than 4.1%) and the intensity pattern of the observed spectrum would appear to verify that H_2InCl is indeed the carrier of the spectrum. Table 8 compares the IR absorptions observed for H_2GaCl[18] and H_2InCl.

The absence of any features arising from HDInCl following the reaction of InCl with a mixture of H_2 and D_2 clearly indicates that H_2 undergoes oxidative addition in a concerted bimolecular reaction. This change almost certainly starts from a contact pair InCl···H_2,[46] and its comparative efficiency suggests a degree of prior interaction between the components of that pair. The failure to detect any sign of this interaction in the infrared spectrum of the matrix prior to photolysis does not rule out the possibility of a weak charge-transfer interaction resulting in the development of a new absorption band in the UV or visible spectrum of a matrix in which InCl and an excess of H_2 are entrapped together. Although we lack the direct spectroscopic signs of initial complex formation that the GaCl/HCl[17,26] and InCl/HCl systems provide, there is circumstantial evidence that loosely bound dihydrogen complexes MCl···H_2 (M = Ga[18] or In) are the vehicles for the photooxidation of MCl to H_2MCl.

Table 9. Normal Coordinate Analysis for $HInCl_2/DInCl_2$ and Comparison with the Frequencies (in cm^{-1}) and Force Constants (in mdyn/Å) Calculated by DFT Methods

	$HInCl_2$			$DInCl_2$		
mode	ν_i	ω_i	calcd	ν_i	ω_i	calcd
$\nu_1(a_1)$	1846.9	1913.9	1913.9	1325.6	1359.6	1359.6
$\nu_2(a_1)$	369.1	369.1	369.1	368.8	368.8	368.8
$\nu_3(a_1)$	102[a]	102	102.0	102[a]	102	102.0
$\nu_4(b_1)$	402.6	402.6	409.6	304.8	304.8	299.4
$\nu_5(b_2)$	469.7	*b*	*b*	311.2	*b*	*b*
$\nu_6(b_2)$	358.5	*b*	*b*	385.1	*b*	*b*

[a] Calculated value. [b] See text. R = In−H, r = In−Cl, α = H−In−Cl, β = Cl−In−Cl, $S_1 = \delta R$, $S_2 = \delta r_1 + \delta r_2$, $S_3 = 2\delta\beta - \delta\alpha_1 - \delta\alpha_2$, $S_4 = \gamma$, $S_5 = \delta\alpha_1 - \delta\alpha_2$, $S_6 = \delta r_1 - \delta r_2$. Force constant values (a) *n.c.a.*: F_{11} 2.157, F_{12} −0.036, F_{13} −0.092, F_{22} 2.379, F_{23} 0.003, F_{33} 0.297, F_{44} 0.269; (b) *DFT*: F_{11} 1.952, F_{12} 0.007, F_{13} −0.040, F_{22} 1.892, F_{23} 0.022, F_{33} 0.294, F_{44} 0.208.

As mentioned earlier, the five signals at 3649.3, 1857.2, 810.0, 606.4, and 451.6 cm^{-1}, observed after photolysis, originate from a reaction product of InCl and H_2O. IR spectra of a matrix containing only InCl and H_2O-doped argon gave the same signals following broad-band UV−visible photolysis. In this experiment with H_2O, two additional absorptions were observed at 428.3 and 348.5 cm^{-1}, with intensities too low to be detected in the experiments with H_2. All of the absorptions belong to the same product, presumably HInCl(OH). Results of DFT calculations for HInCl(OH) (calculated IR frequencies: 3918.8, 1837.4, 675.1, 515.2, 456.3, 453.5, 340.8, 324.9, and 139.6 cm^{-1}; geometry: r(In−Cl) 2.3887 Å, r(In−H) 1.6981 Å, r(In−O) 1.8619 Å, Cl−In−H 120.9°, H−In−O 123.1°, In−O−H 141.3°) support this assignment. It is probably a reflection of the acidity of HCl, which encourages the reaction with InCl, that HInCl(OH) is not sighted in the experiments with InCl and HCl.

Normal Coordinate Analysis Calculations. Normal coordinate analysis calculations have been carried out for the molecules $HInCl_2$ and H_2InCl, using the program ASYM 40.[22] The dimensions have been taken from the DFT-calculated structure as detailed in Table 4. For both molecules the observed frequencies for the fundamentals involving In−H motions have been harmonized using two anharmonicity constants x_i where $\nu_i = \omega_i(1 - x_i)$; these are $x_i = 0.035$ for In−H stretching and $x_i = 0.020$ for InH_2 angle deformation. For the other isotopic species Dennison's rule[47] was applied such that $x'_i = x_i\nu'_i/\nu_i$. Such an approach has proved successful in the analysis of the vibrational spectrum of $[H_2GaCl]_2$.[48] The symmetry coordinates used in the refinement are given in Tables 9 and 10 along with the values obtained for the force constants. It has not proved

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Table 10. Normal Coordinate Analysis for $H_2InCl/D_2InCl/HDInCl$ and Comparison with Frequencies (in cm^{-1}) and Force Constants (in mdyn/Å) Calculated by DFT Methods[a]

	H_2InCl			HDInCl			D_2InCl		
mode	ν_i	ω_i	calcd	ν_i	ω_i	calcd	ν_i	ω_i	calcd
$\nu_1(a_1)$	1804.0	1869.4	1869.7	1301.0	1334.4	1334.2	1291.9	1325.0	1324.5
$\nu_2(a_1)$	575.8	587.6	587.0	523.4	533.0	532.2	415.3	421.2	422.4
$\nu_3(a_1)$	343.4	343.4	344.2	348.5	348.8	347.2	339.3	339.3	340.1
$\nu_4(b_1)$	541.4	541.4	542.5	475.0	475.0	472.5	389.1	389.1	390.1
$\nu_5(b_2)$	1820.3	1886.3	1886.3	1811.1	1876.8	1878.1	1310.9	1344.5	1344.1
$\nu_6(b_2)$	415.7	415.7	414.8	326.9	326.9	325.5	298.2	298.2	300.4

[a] R = In−Cl, r = In−H, α = H−In−Cl, β = H−In−H, $S_1 = \delta r_1 + \delta r_2$, $S_2 = 2\delta\beta - \delta\alpha_1 - \delta\alpha_2$, $S_3 = \delta R$, $S_4 = \gamma$, $S_5 = \delta r_1 - \delta r_2$, $S_6 = \delta\alpha_1 - \delta\alpha_2$. Force constant values (a) *n.c.a.*: F_{11} 2.0689, F_{12} 0.0459, F_{13} −0.0348, F_{22} 0.1980, F_{23} 0.0139, F_{33} 1.8896, F_{44} 0.1646, F_{55} 2.0817, F_{56} −0.0255, F_{66} 0.2863; (b) *DFT*: F_{11} 1.8874, F_{12} 0.0634, F_{13} 0.0367, F_{22} 0.2283, F_{23} −0.0795, F_{33} 1.6986, F_{44} 0.1554, F_{55} 1.8818, F_{56} 0.0356, F_{66} 0.2924.

possible to refine the force constants associated with the b_2 modes of $HInCl_2$. The reason for this lies in the highly coupled nature of the two motions which makes it impossible to correct for anharmonicity in the H motion. Furthermore, the degree of coupling will naturally vary between the different isotopomers. This coupling also gives rise to the unexpected values obtained for the isotopic shifts, made apparent by a comparison of the observed and DFT-calculated frequencies (see Table 5).

To allow for comparison, the Cartesian force constants resulting from the DFT calculations have been transformed to a set of constants corresponding to the symmetry coordinates. On the evidence of Tables 9 and 10 the values are in reasonable agreement.

Other Routes to $HInCl_2$ and H_2InCl. As part of our studies of the reactions of indium atoms and their aggregates,[19] we have sought alternative routes to the mono- and dichloro derivatives of InH_3 by exploring the effect of co-condensing the metal vapor with HCl and an excess of argon and then photolyzing the resulting matrix. Other than the infrared bands associated with HCl and its aggregates[27] and traces of the usual impurities, the condensate initially formed displayed a broad band at 290 cm^{-1} attributable to InCl, thus revealing the fact that the HCl bond is cleaved thermally. Besides the signal belonging to InCl, there was no other sign of a reaction product. Subsequent photolysis with broad-band UV−visible radiation (λ = 200−800 nm) caused the appearance of the bands belonging to $HInCl_2$, while the signal at 290 cm^{-1} belonging to InCl decreased. InCl gives a strong absorption in the UV−visible spectrum near 360 nm. This signal was also used to follow the formation of InCl on deposition and its partial consumption on photolysis. Under similar conditions, In atoms react with H_2 or CH_4 to form initially the In^{II} species RInH (R = H[14,19] or CH_3[15]). By contrast, the reaction with HCl gave no sign of HInCl, possibly because of its photolability under the conditions of our experiments. Although the formation of InCl could not be mistaken, the analogous indium(I) hydride InH was not in evidence,[14] and there was no sign either of H_2InCl. Hence the H−Cl bond is cleaved to give InCl and (presumably) H• atoms, followed by photoactivated addition of HCl to the InCl:

$$\mathrm{In} + \mathrm{HCl} \xrightarrow{\Delta} \mathrm{InCl} + \mathrm{H}\bullet \qquad (4a)$$

$$\mathrm{InCl} + \mathrm{HCl} \xrightarrow{h\nu} \mathrm{HInCl_2} \qquad (4b)$$

Similar studies carried out with gallium and HCl revealed some intriguing differences of behavior. On deposition, a matrix formed by co-condensing gallium vapor with HCl-doped argon displayed, in addition to the expected infrared absorptions, a band at 1513.8 cm^{-1} clearly attributable to the diatomic GaH[14] and others at 342/336 and 303/299 cm^{-1} attributable to GaCl and GaCl···HCl, respectively.[17,26] Photolysis of the matrix with either UV or broad-band UV−visible light then results in the decay of these new features, with the simultaneous appearance and growth of the signatures characteristic of both $HGaCl_2$[17] and H_2GaCl.[18] Hence, it appears that GaH, as well as GaCl, is amenable to photoactivated addition of HCl, thereby providing a second route to H_2GaCl. A possible sequence for the reactions thus seen to occur is set out in eq 5:

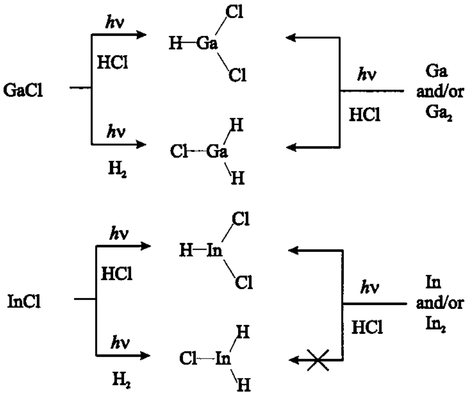
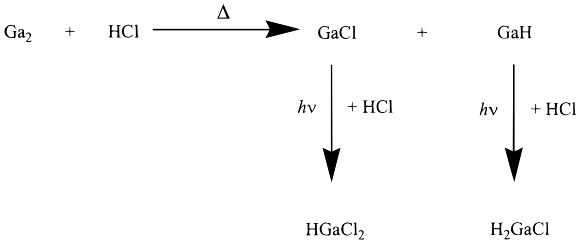


Figure 4. Reaction scheme showing the two different routes to $HMCl_2$ and H_2MCl (M = Ga or In).



(5)

Figure 4 sets out overall reaction schemes summarizing the routes giving access to molecules of the type H_nMCl_{3-n} (M = Ga or In; n = 1 or 2). Hence, we note that the gallium compounds can be produced together by photolysis of the matrices formed by co-depositing gallium vapor with HCl or individually by photolysis of GaCl in the presence of either HCl or H_2. Under similar conditions, however, matrices containing indium vapor species and HCl yield only $HInCl_2$ on photolysis, although $HInCl_2$ and H_2InCl can be made separately by photolysis of InCl/HCl and InCl/H_2 mixtures, respectively. The difference between gallium and indium thus revealed probably hinges on differences in photolability or reactivity of the intermediates.

Conclusions

A matrix-isolation study has been carried out to explore the reactions that occur when InCl is co-condensed with HCl or

H_2 in an argon matrix, and the resulting deposit is irradiated with broad-band UV−visible light (λ = 200−800 nm). The various products have been identified and characterized by their infrared spectra. The response of the spectra to replacing HCl by DCl and H_2 by D_2 and to the natural presence in one or both of the reagents of ^{35}Cl and ^{37}Cl and analogies with the behaviors of AlCl[16] and GaCl[17,18] under similar conditions have both played important roles in assessing the stoichiometries and likely structures of the products. In addition, DFT calculations have been exploited to investigate the optimum geometries and test the inferences drawn from the experiments by simulating the vibrational properties of the principal species involved.

Co-deposition of InCl with HCl gives rise to an identifiable loosely bound adduct InCl···HCl broad-band UV−visible photolysis of which gives access to the indium(III) hydride $HInCl_2$. Molecular pairs of InCl and H_2, which probably represent an even more loosely bound dihydrogen complex, respond similarly to photolysis with the formation of the corresponding monochloro derivative of indane, H_2InCl. As forecast by the DFT calculations, both the products have planar structures with C_{2v} symmetry, and the computed infrared spectra anticipate well the spectra observed for the matrix-isolated products. Five of the six vibrational fundamentals of $HInCl_2$ and all six of the fundamentals of H_2InCl have thus been identified by experiment. Normal coordinate analysis of the observed frequencies confirms the findings, with force constants close to those predicted by the DFT methods. These and other properties of the new molecules invite comparison with the corresponding properties of InH_3,[14] $InCl_3$,[49] and related compounds of the lighter group 13 metals.

When similar methods are applied to study the matrices formed by co-condensing the metal vapor with HCl and an excess of argon, indium is found to behave differently from gallium. Indium reacts thermally with HCl to give InCl and hydrogen atoms. Photolysis then gives $HInCl_2$. With gallium, both GaCl and GaH are observed to be formed at the outset, possibly through the thermally activated reaction of Ga_2 with HCl; thereafter, photoactivated oxidative addition of HCl occurs, to GaH giving H_2GaCl and to GaCl giving $HGaCl_2$.

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