

COORDINATION COMPOUNDS OF INDIUM

XIV*. THE INSERTION OF INDIUM(I) IODIDE INTO CARBON-IODINE BONDS

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SUMMARY

Alkylindium(III) diiodides can be conveniently prepared in high yield by the insertion of indium(I) iodide into the C-I bond of alkyl iodides. The products are halogen-bridged neutral dimers, except for the methyl compound, which is believed to be $[(\text{CH}_3)_2\text{In}][\text{InI}_4]$ in the solid state. One of the intermediates isolated from the reaction mixture is $(\text{CH}_3)_2\text{InI}_2\text{InI}(\text{CH}_3)$; the vibrational spectrum of this compound, and of $(\text{CH}_3)\text{InI}_2\text{InI}_2$, have been investigated. The mechanism of the initial reaction, and the subsequent rearrangement processes, are discussed.

INTRODUCTION

Although the organometallic chemistry of boron and the Group IIIA elements has been a fruitful field of research in recent years, indium is the least explored element of the Group in this respect¹, and even such simple species as the alkylindium(III) halides have only been reported recently²⁻⁴. During work on the coordination chemistry of indium with bidentate ligands, indium(I) halides were shown⁵ to react with 1,2-bis(trifluoromethyl)dithietene (L) to give indium(III) dithiolato complexes $\text{In}^{\text{III}}(\text{L}^{2-})\text{X}$, whose chemistry is typical of that of similar unambiguous indium(III) species⁶. It therefore seemed worthwhile to investigate other possible oxidative insertion reactions of the indium(I) halides, and we now report the results of the first of these studies, the reaction:



with $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{ or } n\text{-C}_4\text{H}_9$

Similar reactions involving the lower oxidation states of Group IVA (*e.g.*, germanium⁷, tin⁸) have been known for some time, although they have not been generally classified as insertion reactions. An analogous reaction to (1), involving indium-

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(I) bromide, has recently been independently reported by Waterworth and Worrall⁹. It appears that insertion reactions may be an important feature of the preparative chemistry of the main group metals, especially since metal-metal bonds to transition-metal carbonyl residues can be obtained in this way¹⁰.

Clark and Pickard³ have reported the synthesis of methylindium(III) dichloride by two routes, using either the reaction of trimethylindium with two moles of hydrogen chloride, or the redistribution reaction between indium(III) chloride and dimethylindium(III) chloride, and we have used the second of these reactions to prepare methylindium(III) dibromide for structural comparisons. In addition to preparing the alkylindium(III) diiodides referred to above, we have investigated the mechanism of the reaction and have isolated a number of intermediates from incompletely reacted mixtures. The structures of these species are discussed in terms of their vibrational spectra. An interesting conclusion of these structural investigations is that methylindium diiodide is an ionic dimer $[(CH_3)_2In][InI_4]$ in the solid state, and hence an example of a stable compound containing the dimethylindium cation, first identified by Hobbs and Tobias¹¹.

EXPERIMENTAL

Spectroscopic and analytical techniques were as described in earlier work¹². Conductivity measurements were made with a "Radiometer" CDM-2d instrument.

Preparative methods

Indium(I) iodide. Indium metal (3.0 g, 0.026 g-atom), was heated (250°) with iodine (10.0 g, 0.078 moles), in a sealed tube for 4 h, after which the tube was opened under nitrogen and indium metal (6.2 g, 0.054 g-atom), added. The tube was resealed and heated at 450° for 24 h. The resulting purple compound was finely ground, the nodule of excess indium metal removed, and the product washed with ether, dried, and stored in the dark under nitrogen. Yield 18.6 g (97%). (Found: I, 52.7; In, 47.7. InI calcd.: I, 52.5; In, 47.5%.)

Methylindium diiodide. Excess methyl iodide (10 ml) was added to finely ground indium(I) iodide (0.452 g), and stirred at 25°. After approximately one hour the monoiodide dissolved to give a clear solution. Excess methyl iodide was removed under vacuum and the remaining white solid dissolved in ether, the solution filtered, and excess ether removed. The resulting white powder was washed with petroleum ether and dried to give methylindium diiodide (0.702 g, 98%), m.p. 125–128° (dec.). (Found: C, 3.23; H, 0.74; I, 66.4; In, 30.1. CH_3I_2In calcd.: C, 3.13; H, 0.79; I, 66.2; In, 29.9%.)

Ethylindium diiodide. The method described above was employed, using excess ethyl iodide (10 ml) and indium(I) iodide (0.396 g), and a reaction temperature of 60° (1 h). The product (0.625 g, 96%), was obtained as a white powder, m.p. 92–94° (dec.). (Found: C, 6.33; H, 1.33; I, 64.1; In, 29.0. $C_2H_5I_2In$ calcd.: C, 6.04; H, 1.27; I, 63.8; In, 28.9%.)

n-Butylindium diiodide. Following the same procedure, butyl iodide (10 ml) and indium(I) iodide (0.516 g) were heated at 50° until the monoiodide dissolved (1–3 h). n-Butylindium diiodide (0.905 g, 89%), m.p. 53°, was obtained. (Found: C, 11.37; H, 2.20; I, 59.8; In, 27.0. $C_4H_9I_2In$ calcd.: C, 11.28; H, 2.13; I, 59.6; In, 26.9%.)

Investigation of other reaction products

Reaction of indium(I) iodide with a small excess of methyl iodide (in contrast to the large excess used preparatively) resulted in the initial formation of a yellow precipitate. Two experiments demonstrated the complex nature of this material. In the first, methyl iodide (2 ml) and indium(I) iodide (0.402 g) were stirred at 25° until the purple colour of the indium monoiodide had just disappeared. The resulting yellow precipitate was immediately filtered off and identified by Raman and infrared spectroscopy¹³ as indium diiodide (0.266) g. (Found: I, 68.4; In, 30.8. InI_2 calcd.: I, 68.9, In, 31.1%.) The filtrate from this reaction was shown by vibrational spectroscopy to contain a mixture of solutes whose principal component was methylindium(III) diiodide.

In the second experiment, using methyl iodide (2 ml) and indium(I) iodide (0.624 g), the reaction product was filtered off before all the indium(I) iodide had dissolved (1 h). The residue was shown to be a mixture of purple indium monoiodide and the yellow diiodide. Immediate removal of excess methyl iodide from the filtrate gave a yellow powder; treatment of this with ether yielded a precipitate of indium(I) iodide, which was removed by filtration. Ether was then distilled from the filtrate, leaving a white powder which was shown to be a mixture of methylindium diiodide and the di- μ -iodo-iodo(trimethyl)diindium(III).

Reaction of methyl iodide and indium diiodide

Excess methyl iodide (10 ml) was added to finely ground indium diiodide (0.921 g) and stirred at 25° (1 h). Removal of excess methyl iodide from the resulting clear solution gave the previously unknown di- μ -iodo-triiodo(methyl)diindium(III) (1.010 g, 100%), m.p. 141°, as a bright yellow solid. (Found: C, 1.51; H, 0.37; I, 72.0; In, 25.9; $\text{CH}_3\text{I}_5\text{In}_2$ calcd.: C, 1.37; H, 0.34; I, 72.2; In, 26.1%.)

Reaction of methylindium diiodide and indium triiodide

The two reactants were mixed in a 1/1 molar ratio in ether and stirred for 48 h. Di- μ -iodo-triiodo(methyl)diindium(III) was formed quantitatively and identified by its m.p., infrared and Raman spectra.

Reaction of dimethylindium iodide and indium triiodide

Equimolar quantities of both reactants were stirred together in ether for 48 h. Methylindium diiodide, m.p. 125–128°, was obtained in quantitative yield after removal of solvent, and identified by its infrared and Raman spectra.

Reaction of dimethylindium iodide and methylindium diiodide

The two substances were stirred together in ether for 48 h (1/1 mole ratio). Removal of ether gave di- μ -iodo-iodo(trimethyl)diindium(III), m.p. 90–100° dec. as a white powder in quantitative yield. (Found: C, 5.62; H, 1.41; I, 57.6; In, 34.8. $\text{C}_3\text{H}_9\text{I}_3\text{In}_2$ calcd.: C, 5.50; H, 1.38; I, 58.0; In, 35.0%.)

Preparation of methylindium dibromide

Indium tribromide and dimethylindium bromide were mixed in equimolar quantities in ether, and the mixture stirred for 48 h. Methylindium dibromide, m.p. 164°, was produced quantitatively. (Found: C, 4.32; H, 1.00; In, 40.0. $\text{CH}_3\text{Br}_2\text{In}$

calcd.: C, 4.15; H, 1.04; In 39.6%) Methylindium(III) dichloride was prepared in a similar manner, following Clark and Pickard³.

Reaction of indium(I) bromide and benzyl bromide

Indium monobromide (0.03 g) and benzyl bromide (2.86 g) were stirred together at 0°. After approximately 2½ h, a sudden reaction resulted in the formation of an orange solid, and the evolution of gas (shown to be HBr by its mass spectrum) (248 ml, 90%). The orange solid, believed to be mainly a polymer (C₆H₅CH)_n, was insoluble in all common solvents. (Found: C, 87.3; H, 6.59%) Allyl bromide reacted similarly.

DISCUSSION

The structures of alkylindium diiodides

The most useful techniques for investigating the structure of organoindium iodides are vibrational spectroscopy of solids, measurements of the conductivity of dilute solutions in solvents such as nitromethane, and mass spectrometry. We note

TABLE 1

MASS SPECTRA OF ALKYLINDIUM(III) DIIODIDES AND RELATED COMPOUNDS

| <i>Compound</i> | <i>Sample temp. (°C)</i> | <i>Predominant peaks</i> | <i>Other significant peaks</i> |
|---|--------------------------|---|---|
| CH ₃ InI ≡[(CH ₃) ₂ In][InI ₂] | 95 | 257 CH ₃ InI 369 InI ₂ 384 CH ₃ InI ₂ 145 (CH ₃) ₂ In | 496 InI ₃ 641 (CH ₃) ₂ InI ₃ 753 CH ₃ In ₂ I ₄ |
| (C ₂ H ₅ InI ₂) ₂ | 110 | 271 C ₂ H ₅ InI 369 InI ₂ 398 C ₂ H ₅ InI ₂ | 156 C ₂ H ₅ I 173 (C ₂ H ₅) ₂ In 496 InI ₃ 768 C ₂ H ₅ In ₂ I ₄ 669 (C ₂ H ₅) ₂ InI ₃ 611 In ₂ I ₃ |
| (n-C ₄ H ₉ InI ₂) ₂ | 150 | 299 C ₄ H ₉ InI 369 InI ₂ | 183 C ₄ H ₉ I 426 C ₄ H ₉ InI ₂ 496 InI ₃ 795 C ₄ H ₉ In ₂ I ₄ 725 (C ₄ H ₉) ₂ In ₂ I ₃ 611 In ₂ I ₃ |
| (CH ₃) ₂ InI ₂ InI(CH ₃) | 130 | 257 CH ₃ InI 145 (CH ₃) ₂ In 369 InI ₂ 130 CH ₃ In 384 CH ₃ InI ₂ | 553 C ₄ H ₉ In ₂ I ₃ 641 (CH ₃) ₂ In ₂ I ₃ 529 (CH ₃) ₃ In ₂ I ₂ |
| I ₂ InI ₂ InI(CH ₃) | 160 | 257 CH ₃ InI 369 InI ₂ 496 InI ₃ 384 CH ₃ InI ₂ 142 CH ₃ I | 753 CH ₃ In ₂ I ₄ 865 In ₂ I ₅ 626 CH ₃ In ₂ I ₃ 611 In ₂ I ₃ |

that from such experiments, Clark and Pickard³ showed that CH_3InCl_2 is a monomer in nitromethane; $(\text{CH}_3)_2\text{InCl}$ and $(\text{CH}_3)_2\text{InI}$ are, however, both dimeric in benzene.

Table 1 summarises the results of mass-spectrometric studies of the three alkylindium(III) iodides prepared in this work.

In addition to the ions listed, each compound gave rise to prominent In^+ , I^+ and InI^+ peaks, and a large number of ions with $m/e < 100$. The results show that dimeric species are present in the vapour phase since RIn_2I_4^+ and R_2InI_3^+ ions are found, although the parent ion $\text{R}_2\text{In}_2\text{I}_4^+$ was not detected in any of the spectra. The highest intensity peaks above $m/e \sim 100$ are InI_2^+ and RInI^+ , with the R_2In^+ ion only being important in the $\text{R} = \text{CH}_3$ case. We have found that the most important species in the mass spectra of the indium(III) halides is always InX_2^+ , even though dimeric species also exist in these systems¹⁴. These InX_2^+ , RInX^+ , etc. cations are isoelectronic with the known neutral cadmium(II) molecules¹⁵. On the basis of the results in Table 1 we therefore conclude that the RInI_2 compounds are all dimeric in the vapour phase, and probably also in the solid state.

The vibrational spectra of the $(\text{RInI}_2)_2$ compounds in the $\nu(\text{In}-\text{C})$, $\nu(\text{In}-\text{I})$ and related regions are shown in Table 2. It is immediately obvious that the methyl compound is different from the other two prepared, in that there are two $\nu(\text{In}-\text{C})$ modes, with frequencies close to the values of $500(\text{Raman}) + 566(\text{IR}) \text{ cm}^{-1}$ reported by Hobbs and Tobias¹¹ for $[(\text{CH}_3)_2\text{In}]^+$, which these authors obtained by the low temperature hydrolysis of $(\text{CH}_3)_2\text{InCl}$. In keeping with this, the $\text{In}-\text{I}$ vibrations are in good agreement with those for the InI_4^- anion in a symmetry lower than T_d . In a comparable case, the Raman spectrum of $\text{In}[\text{InI}_4]$ (*i.e.*, indium diiodide)¹³ has bands

TABLE 2

VIBRATIONAL SPECTRA OF ALKYLINDIUM(III) DIHALIDES, AND MOLAR CONDUCTIVITIES IN NITROMETHANE

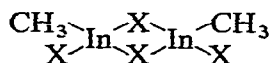
| Compound | Infrared (cm^{-1}) | | Raman (cm^{-1}) | | Molar Conductivity (mM concn.) ($\text{ohm}^{-1} \cdot \text{cm}^2$) |
|--|-------------------------------|---------------------------|----------------------------|---|--|
| | <i>In-CH₃ rock</i> | $\nu(\text{In}-\text{C})$ | $\nu(\text{In}-\text{C})$ | $\nu(\text{In}-\text{I})$ etc. | |
| $[(\text{CH}_3)_3\text{In}][\text{InI}_4]$ | 755 s(br) | 561 s | 483 s | 196 w 184 m 141 vs 73 vw 64 m 44 m | 65 |
| $(\text{C}_2\text{H}_5\text{InI}_2)_2$ | | 490 s | 489 s | 170 m 144 s 61 w | 27 ^a |
| $(n\text{-C}_4\text{H}_9\text{InI}_2)_2$ | | 489 m | 487 m | 169 m 141 s(br) 66 vw | 25 ^a |
| $\text{CH}_3\text{InCl}_2^c$ | 750 s(br) | 526 s 523 m(br) | 527 s | | 13.3 ^b |
| CH_3InBr_2 | 735 s(br) | 526 s | 522 s | | 21.8 ^a |

^a Conductivity increases with time; the values quoted are for freshly prepared solutions (*cf.* text). ^b Data from ref. 3. ^c Prepared by the method of Clark and Pickard (ref. 3).

at 191 w, 177 vw, 138 vs, 72 vw, 62 w and 47 m cm^{-1} , in contrast with the spectrum of the InI_4^- anion in non-aqueous solution¹⁶ (ν_1 139 vs, ν_3 185 w(br) and ν_4 58 cm^{-1}). We therefore conclude that $(\text{CH}_3\text{InI}_2)_2$ is most probably the ionic dimer $[(\text{CH}_3)_2\text{In}][\text{InI}_4]$, with the vibrations at 483 and 561 cm^{-1} assigned as ν_{sym} and ν_{as} of the cation.

The occurrence of crystalline ionic dimers is an interesting feature of the coordination chemistry of indium(III). Two closely related examples are the adduct "InI₃ · 2DMSO" (DMSO = dimethylsulphoxide), which has the structure¹⁷ $[\text{InI}_2(\text{DMSO})_4][\text{InI}_4]$, and indium diiodide, which has been shown to be $\text{In}[\text{InI}_4]$ ¹³. One important factor in these structures, and in the present case, must be the thermodynamic stability of the InI_4^- anion, which is the only anion obtained in studies of anionic indium(III) complexes with a variety of cations¹⁸.

The compounds $(\text{C}_2\text{H}_5)\text{InI}_2$ and $n\text{-C}_4\text{H}_9\text{InI}_2$ have only one $\nu(\text{In-C})$ mode, as has (monomeric) CH_3InCl_2 and $(\text{CH}_3\text{InBr}_2)_2$ so that each of the dimers must be of the type:



This is in keeping with the mass spectrometric evidence, in that R_2In^+ ions are much less abundant than RInI^+ species, except in the case of $\text{R} = \text{CH}_3$; presumably some intermolecular rearrangements occur in the sample chamber of the mass spectrometer, giving rise to small amounts of $\text{R}_2\text{InI}_2\text{InI}_2$, etc. The assignment of $\nu(\text{In-I})$ modes depends on the work of Greenwood *et al.*^{19,20} on $\text{I}_2\text{InI}_2\text{InI}_2$, and on an earlier assignment⁶ for the salt $[(\text{C}_2\text{H}_5)_4\text{N}][\text{In}(\text{i-MNT})_2\text{I}]$ (i-MNT = 1,1-dicyanoethylene-2,2-dithiolate), for which $\nu(\text{In-I})$ is at 167 cm^{-1} . The strongest band in the Raman spectrum of In_2I_6 is at 135 cm^{-1} , the breathing vibration of the $\text{In} \begin{array}{c} \diagdown \quad \diagup \\ \diagup \quad \diagdown \end{array} \text{In}$ ring, and we therefore assign the lines at 144 ($\text{R} = \text{C}_2\text{H}_5$) and 141 cm^{-1} ($\text{R} = n\text{-C}_4\text{H}_9$) to this mode with the bands at 170 and 169 cm^{-1} arising from $\nu(\text{In-I})$ of the terminal iodine.

The conductivity of $[(\text{CH}_3)_2\text{In}][\text{InI}_4]$ in nitromethane is similar to, but slightly lower than, that reported for other 1/1 electrolytes in this solvent⁶, and clearly higher than for the other compounds investigated. For these latter species, the conductivities increase with time, and it seems likely that this is the result of rearrangement reactions, such as:

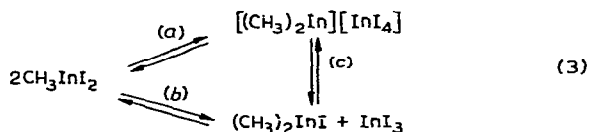


By contrast, solutions of $[(\text{CH}_3)_2\text{In}][\text{InI}_4]$ in nitromethane are stable. Rearrangement processes such as (2), involving change of coordination number in solution are a common feature of the chemistry of adducts of neutral donors with indium halides²¹ and organoindium halides²².

The insertion reaction and subsequent rearrangements

Reaction (1) obviously involves a heterogeneous mixture, which in the presence of a large excess of (say) methyl iodide finally goes to a clear solution. Intermediate stages are implied by the colour change of the solid phase (white \rightarrow yellow) observed with smaller quantities of methyl iodide, and by the identification of InI_2 , InI_3 , $(\text{CH}_3)_2\text{InI}_2\text{InI}(\text{CH}_3)$ and (by implication) $\text{I}_2\text{InI}_2\text{InI}(\text{CH}_3)$ in the reaction mixtures (see Experimental).

It is suggested that the first step is the direct attack of CH_3I at the surface of InI to give CH_3InI_2 , which is unstable as the monomer. Two related equilibria can be written for the dimerisation:



As noted above [eqn. (2)], such equilibria are similar to those proposed earlier to explain rearrangements in solutions of indium halide adducts²¹. The thermodynamic stability of the anion and cation results in the ionic dimer being the favoured species in the solid state.

If the amount of methyl iodide is lowered, a yellow solid, identified as InI_2 , is formed by the reaction of InI_3 [produced via 2(b)] with InI . In a parallel process, $(\text{CH}_3)_2\text{InI}$, also formed via reaction 2(b), reacts with the unstable monomer CH_3InI_2 (or one of its derivatives) to form $(\text{CH}_3)_2\text{InI}_2\text{InI}(\text{CH}_3)$ which can be isolated from the mixture (see Experimental). Prolonged treatment of mixtures with methyl iodide eventually converts all these species to $[(\text{CH}_3)_2\text{In}][\text{InI}_4]$; the compound $\text{I}_2\text{InI}_2\text{InI}(\text{CH}_3)$ must also be postulated as an intermediate since this can be formed from CH_3I and InI_2 . The equilibria set out in (3) above can then be invoked to explain the formation of all the species isolated from the reaction mixture. For the $\text{R} = \text{C}_2\text{H}_5$ and $n\text{-C}_4\text{H}_9$ reactions, these equilibria are presumably also established (*cf.* conductivity results in Table 1), but the stable solid state species is now the neutral dimer.

We were unable to obtain evidence of any reaction between indium(I)iodide and iodobenzene over a short period of time, and it seemed possible that the C-I bond strength might be a critical factor in the reaction scheme, since the reported²³ C-I bond energies are CH_3I 54; $\text{C}_2\text{H}_5\text{I}$ 51; $\text{C}_4\text{H}_9\text{I}$ 49; $\text{C}_6\text{H}_5\text{I}$ 61 kcal. We therefore attempted the reaction of InBr with $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ and $\text{CH}_2=\text{CH}-\text{CH}_2\text{Br}$, which have weaker C-Br bonds ($D = 50.5$ and 47.7 kcal respectively²³) than do the simple alkyl bromides, but the required RInBr_2 compounds were not obtained. The work of Waterworth and Worrall⁹ suggests that kinetic factors are in fact of greater importance than equilibrium properties such as bond strength, since the reaction of InBr and CH_3Br (bond strength 67 kcal)²³ proceeds, but slowly, at temperatures higher than those used in the present work.

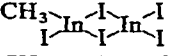
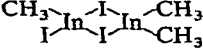
The structures of reaction by-products

The structures of the reaction by-products discussed are well-established, with the exception of $\text{I}_2\text{InI}_2\text{InI}(\text{CH}_3)$ (I) and $(\text{CH}_3)_2\text{InI}_2\text{InI}(\text{CH}_3)$ (II). The mass and vibrational spectra of these compounds are shown in part in Tables 1 and 3. The mass spectra establish the dimeric nature of these two compounds, and the cracking patterns confirm the halogen bridged structures, with one and three terminal methyl groups respectively.

In the vibrational spectra, (Table 3), the single $\nu(\text{In}-\text{C})$ in (I) contrasts sharply with the three bands observed for the trimethyl compound (II). For the latter, the coincident infrared and Raman bands at 508 cm^{-1} are assigned to $\nu(\text{In}-\text{C})$ for the unique terminal methyl group, and the other two $\nu(\text{In}-\text{C})$ modes in this compound are then ν_{as} and ν_{sym} of the Me_2In moiety. Values of 555 and 486 cm^{-1} agree well with

TABLE 3

INFRARED AND RAMAN SPECTRA OF $I_2In_2InI(CH_3)$ AND $(CH_3)_2In_2InI(CH_3)$ (in cm^{-1})

| Compound | CH_3 deformation (IR) | $In-CH_3$ rock (IR) | $\nu(In-C)$ | | $In-I$ (Raman) |
|---|----------------------------|------------------------|-------------------------|----------------|------------------------------------|
| | | | IR | Raman | |
|  | 1145 s | 730 vs(br) | 509 m | 510 m | 216 w, 188 m 140 vs, 108 w |
|  | 1145 m, 1160 mw | 730 vs(br) | 485 w 509 s 555 s | 486 m 508 m | 161 (sh), 152 s 114 m(br), 66 w |

those in dimethylindium iodide (558 and 488 cm^{-1}), which is formulated by Clark and Pickard² as the dimer $(CH_3)_2InI_2In(CH_3)_2$. There are also notable differences in the CH_3 deformation modes in the spectra of the compounds (I) and (II). Any differences in the $In-CH_3$ rocking frequencies must be obscured by the breadth of these bands in the infrared spectrum.

The $In-I$ vibrations cannot be assigned with certainty in the absence of far infrared data, but the data in Table 3 are in keeping with the dimeric structures proposed for (I) and (II). Following the discussion above for $(RInI_2)_2$ ($R=C_2H_5$ or C_4H_9), the intense band at 140 cm^{-1} is identified as the ring breathing mode of the $In\begin{smallmatrix} I \\ | \\ I \end{smallmatrix}In$ group. The two bands at 216 and 188 cm^{-1} have the appropriate relative intensities and splitting to be ν_{as} and ν_{sym} of the terminal $In\begin{smallmatrix} I \\ | \\ I \end{smallmatrix}$ group; in $(CH_3)_2SnI_2$,

the corresponding frequencies²⁴ are 197 and 182 cm^{-1} , and in the dimeric In_2I_6 ($=I_2In_2InI_2$) bands at 214 and 190 have been assigned¹⁹ to the stretching modes of the terminal InI_2 . The weak band at 108 cm^{-1} in (I) cannot be identified at present.

In the trimethyl compound (II), the ring breathing mode is identified with the strongest band at 152 cm^{-1} , with the terminal $\nu(In-I)$ at 161 cm^{-1} . The broad band at 114 cm^{-1} can be tentatively assigned to the $\delta(In-C_2)$ vibration of the terminal $In(CH_3)_2$ group; all three dimethylindium halides have Raman active vibrations at $111 \pm 2\text{ cm}^{-1}$.

ACKNOWLEDGEMENT

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