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# Studies on the Nature of the Dimethylindium(III) Ion and on Some of Its Compounds by Raman, Infrared, and Proton Magnetic Resonance Spectroscopy. Normal Coordinates of the Dimethylindium Ion and Bonding in Dimethylmetal Cations[1,2]

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Raman and infrared spectra have been recorded for aqueous solutions of $(CH_3)_2InCl$ and $(CH_3)_2InClO_4$. For comparison, spectra also were obtained for solid $[(CH_3)_2InCl]_2$, $(CH_3)_2InCl\cdot py$, and $(CH_3)_2In(acac)$ where there is approximately tetrahedral coordination about indium. The spectra of the aquo cation $(CH_3)_2In^+$, which was found to be stable for days in aqueous solution at 0°, have been assigned on the basis of a linear skeleton, and a normal-coordinate analysis using all nine atoms has been carried out. The metal–carbon stretching force constants increase normally in the sequence $(CH_3)_2Cd$, $(CH_3)_2In^+$, and $(CH_3)_2Sn^{2+}$ which is the opposite of the trend from $(CH_3)_2Hg$ to $(CH_3)_2Pb^{2+}$. Consequently, the decrease from mercury to lead cannot be ascribed to solvent effects alone. The carbon–hydrogen stretching force constants increase with increasing positive charge on the species in both of these isoelectronic sequences as do the carbon-13–proton coupling constants. Trends in the bonding in these molecules and ions are discussed on the basis of these data.

## Introduction

The dimethyl derivatives of the posttransition metals have been studied in some detail, and the ions and molecules $(CH_3)_2Cd$ and $(CH_3)_2Sn^{2+}$ which are isoelectronic and $(CH_3)_2Hg$, $(CH_3)_2Tl^+$, and $(CH_3)_2Pb^{2+}$ which also are isoelectronic all have been found to have linear skeletons.[4] In contrast to these ions, the dimethylgallium(III) aquo ion has an angular structure[5] which probably is closely related to that of $(CH_3)_2Ga(NH_3)_2{}^+$.[6] The dimethylgermanium(IV) moiety, isoelectronic with dimethylgallium(III), also has an angular structure in aqueous solution,[7] but it is completely hydrolyzed to $(CH_3)_2Ge(OH)_2$.

Normal-coordinate analyses[4] involving all nine atoms of the $(CH_3)_2M$ ions and molecules have confirmed that the trend in the metal–carbon bond strengths with the heaviest metals is Hg–C > Tl–C > Pb–C which is the opposite of what might be expected. The metal–carbon valence force constants were found to be $2.5_8$, $2.4_3$, and $2.3_0$ mdyn/Å, respectively. This trend was first noted by Goggin in 1960,[8] and it was suggested that there was some mercury 5d orbital participation in the bonds to carbon. An alternate explanation is that there is simply a change in coordination number in going from $(CH_3)_2Hg$ to $(CH_3)_2Pb^{2+}$. Spectra for $(CH_3)_2Hg$ were determined with the neat liquid or vapor, while the spectra for $(CH_3)_2Tl^+$ and $(CH_3)_2Pb^{2+}$ were obtained with aqueous solutions of the nitrate and perchlorate salts. Of the two ions, the dipositive cation should be the most strongly hydrated, and the decrease in metal–carbon stretching force constants from Hg to Pb could simply be a consequence of the binding of water molecules to the metal. As evidence against this argument, the metal–carbon stretching force constant for $(CH_3)_2Sn^{2+}$ is larger than that for $(CH_3)_2Cd$.[4] Of all of the ions studied, the dipositive dimethyltin(IV) species should be the most strongly solvated.

Recently, two extensive investigations[9,10] have been made by Clark and Pickard of dimethylindium(III) compounds. Adducts of the type $(CH_3)_2InXL$, where X is a halide and L a Lewis base, all were found to have tetrahedral coordination about indium. With bidentate ligands like phenanthroline and dipyridyl, it appeared that five-coordinate complexes were formed.

Data on the dimethylindium(III) ion would permit a comparison along the isoelectronic sequence Cd(II), In(III), and Sn(IV). There is conflicting information in the literature about the stability of dialkylindium(III) ions in aqueous solution. Coates, *et al.*,[11] reviewing the literature reported that $(CH_3)_3In$ is vigorously hydrolyzed by cold water with the formation of 2 mol of methane and $CH_3In(OH)_2$. Rochow[12] remarked that indium alkyls lose only one organic group to form $R_2InOH$ by reaction with water at room temperature.

In this communication, we report studies on the vibrational spectra of aqueous solutions containing the dimethylindium(III) cation which was found to be relatively long-lived in solution at 0°. The spectra were collected to ascertain whether the skeleton of $(CH_3)_2In^+$ is angular in aqueous solution like $(CH_3)_2Ga^+$ or linear like $(CH_3)_2Tl^+$. In addition, a normal-coordinate calculation has been carried out to evaluate

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[1] Supported, in part, by the National Science Foundation, Grants GP-5022 and GP-7899, and by the Petroleum Research Fund, Administered by the American Chemical Society.

[2] Taken from a thesis submitted by C. W. H. to the Graduate School of the University of Minnesota for the Ph.D. degree, 1969.

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[4] See, for example, the discussion in M. G. Miles, J. H. Patterson, M. J. Hopper, C. W. Hobbs, J. Overend, and R. S. Tobias, *Inorg. Chem.*, **7**, 1721 (1968).

[5] R. S. Tobias, M. J. Sprague, and G. E. Glass, *ibid.*, **7**, 1714 (1968).

[6] D. F. Shriver and R. W. Parry, *ibid.*, **1**, 835 (1962).

[7] R. S. Tobias and S. Hutcheson, *J. Organometal. Chem.*, **6**, 535 (1966).

[8] P. L. Goggin, Ph.D. Thesis, Oxford, 1960.

[9] H. C. Clark and A. L. Pickard, *J. Organometal. Chem.*, **8**, 427 (1967).

[10] H. C. Clark and A. L. Pickard, *ibid.*, **13**, 61 (1968).

[11] G. E. Coates, M. L. H. Green, and K. Wade, "Organo-Metallic Compounds," Vol. 1, 3rd ed, Methuen, London, p 360.

[12] E. G. Rochow, "Organometallic Compounds," Reinhold, New York, N. Y., 1964, p 51.

the metal–carbon bond strength of $(CH_3)_2In^+$ relative to those of the isoelectronic $(CH_3)_2Cd$ and $(CH_3)_2Sn^{2+}$.

## Experimental Section

**General Data.**—Methyllithium was obtained from Foote Mineral Co. Eastman Organic Chemicals acetylacetone was distilled before use. Melting points were obtained with a Fisher-Johns apparatus under a dry nitrogen atmosphere. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and by Clark Microanalytical Laboratory, Urbana, Ill.

**Dimethylindium Chloride, $(CH_3)_2InCl$.**—The procedure of Clark and Pickard[9] was used, and this involves the addition of $InCl_3$ to methyllithium dissolved in diethyl ether. After reaction, the ether was removed on a vacuum line, and the white product which remained was purified by sublimation under vacuum at 90–100°. *Anal.* Calcd for $C_2H_6ClIn$: C, 13.3; H, 3.32; Cl, 19.7. Found: C, 13.6; H, 3.60; Cl, 19.5; mp 218–219°; lit.[9] mp 218–219°.

**Dimethylindium Chloride–Pyridine, $(CH_3)_2InCl \cdot C_5H_5N$.**—This compound also was prepared as described by Clark and Pickard.[9] The product was stored under vacuum for 36 hr and washed with petroleum ether (bp 60–68°) to remove excess pyridine. *Anal.* Calcd for $C_7H_{11}NClIn$: C, 32.4; H, 4.24; N, 5.39; Cl, 13.7. Found: C, 31.1; H, 4.18; N, 5.06; Cl, 13.1; mp 83–84; lit.[9] mp 72–75°.

**Dimethylindium(III) Acetylacetonate, $(CH_3)_2In(C_5H_7O_2)$.**—Synthesis was by the method of Coates and Whitecombe[13] which involves reaction of $InCl_3$ and $CH_3Li$ in a 1:3 mol ratio followed by the addition at −60° of acetylacetone to react with the $(CH_3)_3In$ produced. The mixture was allowed to warm to room temperature, the ether was removed on the vacuum line, and the product was purified by vacuum sublimation. *Anal.* Calcd for $C_7H_{13}O_2In$: C, 34.6; H, 5.35; O, 13.2. Found: C, 33.3; H, 5.21; O, 14.2; mp 120–125, lit. mp 118°,[13] 170–172°[14] dec.

**Aqueous Solutions.**—Solid $(CH_3)_2InCl$ was dissolved in cold water and kept at 0°. Solutions of $(CH_3)_2In(ClO_4)$ were prepared by adding $(CH_3)_2InCl$ to a cold aqueous solution of $TlClO_4$. The precipitate of TlCl was removed by filtration, and the solution was concentrated to the point of saturation in a vacuum desiccator. The analogous reaction with $AgClO_4$ led to oxidation of the organoindium compound. Solutions of $(CH_3)_2Tl(NO_3)$ were prepared following the procedure of Goddard.[15] In anhydrous methanol, $(CH_3)_2TlI$[16] was allowed to react with $AgNO_3$, and the solution was refluxed for 2 hr. The AgI was removed by filtration, the methanol was evaporated in a stream of nitrogen until the volume was *ca.* 10 ml, diethyl ether was added to precipitate $(CH_3)_2Tl(NO_3)$, and the product was collected on a frit. Weighed samples were dissolved in distilled water. Aqueous solutions of $(CH_3)_2Pb(ClO_4)_2$[17] were prepared by adding $(CH_3)_2PbCl_2$[18] to an aqueous solution of $AgClO_4$. The mixture was stirred for several hours, and the AgCl was removed by filtration.

**Raman Spectra.**—The solution spectra were recorded with a Toronto arc-excited Cary 81 spectrophotometer using a microcell with a capacity of *ca.* 0.1 ml. The 4358-Å mercury line was isolated using a filter solution containing 40 g of Cyasorb UV-24 and 2 g of ethyl violet dissolved per gallon of 2-propanol. Solid spectra were recorded both with the Cary instrument using conical glass cells and also with a laser Raman spectrophotometer which has been described briefly elsewhere.[19] With laser excitation, a thin layer of the powdered sample was illuminated at 90° to the optical axis of the monochromator. Sharp lines are accurate to ±2 $cm^{-1}$.

**Infrared Spectra.**—Perkin-Elmer 521 and Beckman IR-12 spectrometers were used, and calibration was effected with polystyrene film. Solid spectra in the 200–1300-$cm^{-1}$ region were obtained with Nujol mulls using CsI windows, while spectra in the 1300–4000-$cm^{-1}$ region were obtained using NaCl or KBr plates and Halocarbon oil mulls. Aqueous solution spectra were obtained with AgCl plates or polyethylene sheets as windows for thin films of the solution. In general, sharp bands are accurate to ±2 $cm^{-1}$ while broad bands should be within ±5 $cm^{-1}$.

**Proton Magnetic Resonance Spectra.**—A Varian A-60 spectrometer was used. Side bands were produced by a Hewlett-Packard 3300A function generator and a Hewlett-Packard 3734A electronic counter was used to calibrate the frequency. Coupling constants are believed accurate to ±1 Hz.

## Data and Results

Dimethylindium(III) chloride is dimeric in benzene[9] solution and also presumably in the solid state. The likely molecular symmetry, assuming free rotation of the methyl groups, is $D_{2h}$. For such a structure, there are 18 skeletal normal modes,[20,21] and the detailed description of these is an exceedingly difficult problem. Of the 18 modes, only 5 were observed. Assignments for the Raman and infrared spectra are given in Table I. Both spectra are reproduced in Figure 1. Since the molecule is centrosymmetric, there should be mutual exclusion in the Raman and infrared spectra; however, little coupling is to be expected through the heavy indium atoms and the relatively weak di-μ-chloro bridge. The numbering system used in Table I for the skeletal vibrations is that of Bell and Longuet-Higgins.[22,23] Since coupling between the two ends of the molecule is slight, the two Raman-active and two infrared-active vibrations in the 500–600-$cm^{-1}$ region can be qualitatively assigned to symmetric and asymmetric $InC_2$ stretching. The four In–C coordinates transform as $a_g + b_{1g} + b_{2u} + b_{3u}$ (bonds in $xy$ plane). The di-μ-chloro bridge appears to be very weak since no vibration assignable to $InCl_2In$ stretching was observed

TABLE I

INFRARED AND RAMAN FREQUENCIES AND QUALITATIVE ASSIGNMENTS FOR SOLID $[(CH_3)_2InCl]_2$

| $\nu$, $cm^{-1}$ | | |
|---|---|---|
| Ir | Raman | Assignment |
| | 193 w | $InCl_2In$ breathing, $\nu_2$ |
| | 446 w | Scattering from glass |
| 492 m[a] | | $InC_2$ sym str, $\nu_1$ |
| | 500 vvs | $InC_2$ sym str, $\nu_{16}$ |
| | 561 w | $InC_2$ asym str, $\nu_{11}$ |
| 563 s | | $InC_2$ asym str, $\nu_8$ |
| 737 s, b | 726 w | $In–CH_3$ rock |
| 1179 m | 1176 m | $CH_3$ sym def |
| 2923 m | | $CH_3$ sym str |
| | 2924 m | |
| 2999 w | 3005 w | $CH_3$ asym str |

[a] Abbreviations: w, weak; m, medium; s, strong; v, very; b, broad.

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(13) G. E. Coates and R. A. Whitcombe, *J. Chem. Soc.*, 3351 (1956).

(14) C. Z. Moore and W. H. Nelson, *Inorg. Chem.*, **8**, 143 (1969).

(15) A. E. Goddard, *J. Chem. Soc.*, 672 (1921).

(16) We are indebted to Dr. M. J. Sprague for the synthesis of this compound.

(17) C. E. Freidline and R. S. Tobias, *Inorg. Chem.*, **5**, 354 (1966).

(18) We are indebted to Miss Y. M. Chow for this compound.

(19) W. M. Scovell and R. S. Tobias, *Inorg. Chem.*, **9**, 945 (1970).

(20) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963, p 120.

(21) D. M. Adams, "Metal-Ligand and Related Vibrations," Edward Arnold, London, 1967, p 36.

(22) R. P. Bell and H. C. Longuet-Higgins, *Proc. Roy. Soc., Ser. A*, **183**, 357 (1945).

(23) See also the discussion for related $M_2X_6$ and $[(CH_3)_2AlCl]_2$ molecules in ref 20 and 21.

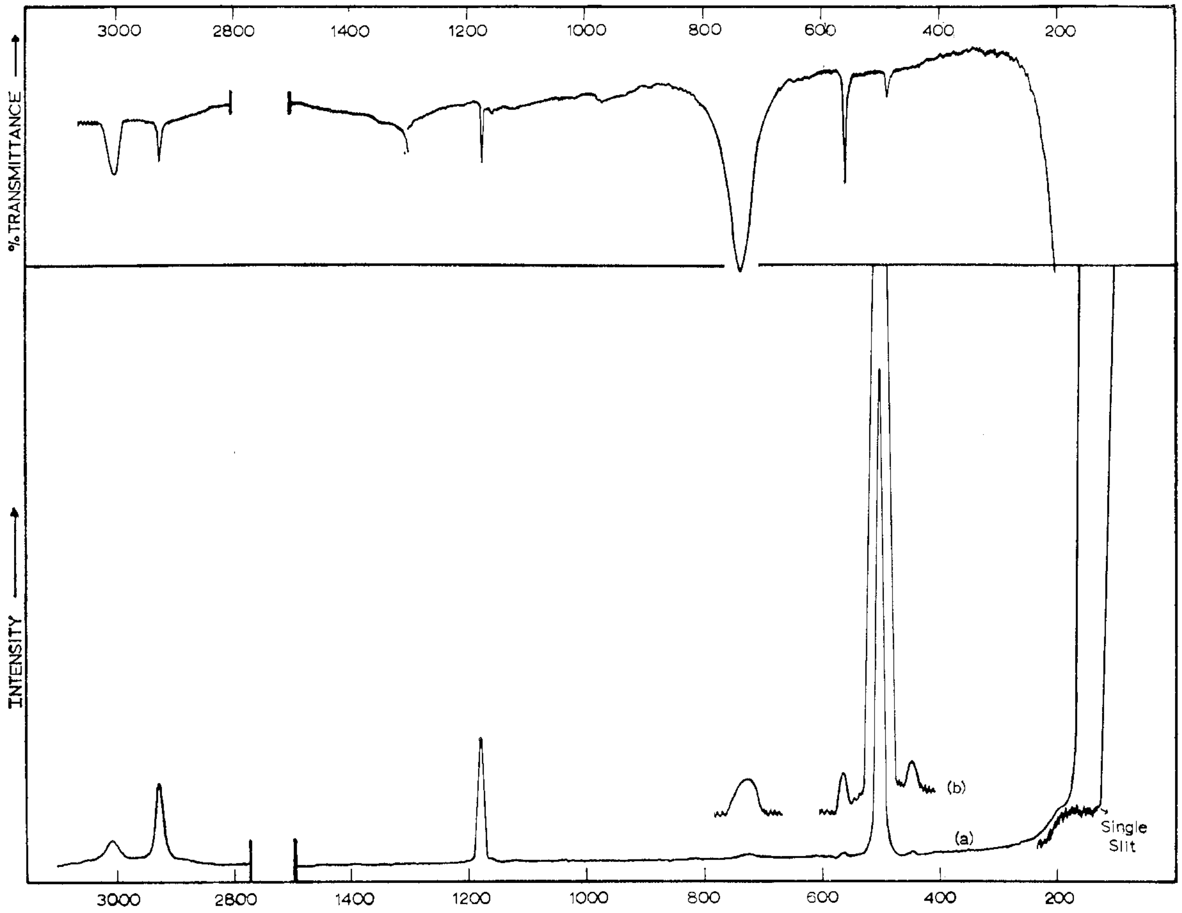

Figure 1.—Raman and infrared spectra of crystalline $[(CH_3)_2InCl]_2$. Sensitivity: (a) 1 × 100; (b) 1 × 1000.

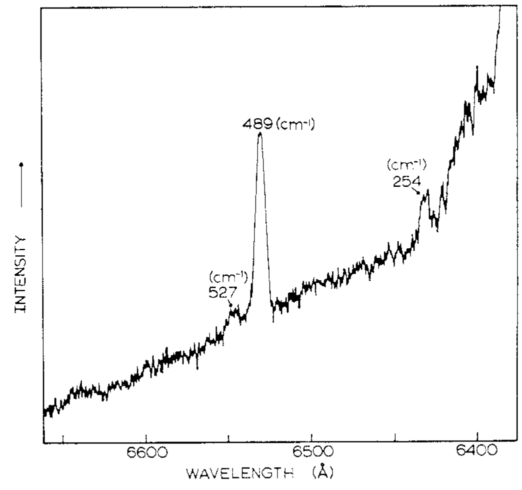

Figure 2.—Laser Raman spectrum of crystalline $(CH_3)_2InCl \cdot py$.

above 200 cm$^{-1}$. The four InCl coordinates transform as $a_g + b_{2g} + b_{1u} + b_{3u}$. It is probable that the broad band in the Raman spectrum centered at *ca.* 193 cm$^{-1}$ is due to the $a_g$ and $b_{2g}$ modes. The weak Raman scattering at 446 cm$^{-1}$ was caused by the conical glass cell used to record the spectrum.

Destruction of the di-$\mu$-chloro bridge by coordination of pyridine to the chloride to yield $(CH_3)_2InCl \cdot py$ leads to the appearance of the simple symmetric and asymmetric $InC_2$ stretching modes at a somewhat lower frequencies than in the binuclear chloride—489 (R),

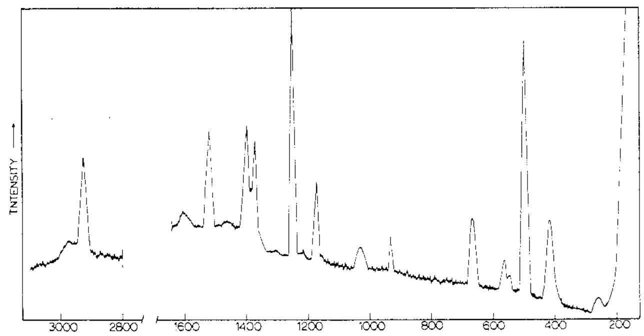

Figure 3.—Raman spectrum of crystalline $(CH_3)_2In(acac)$.

489 (ir) as well as to 527 (R) and 529 cm$^{-1}$ (ir). A band assigned to InCl stretching is observed in the Raman spectrum at 254 cm$^{-1}$ and in the infrared spectrum at 264 cm$^{-1}$. Vibrations due to coordinated pyridine[24] are observed in the infrared spectrum at 414 (m), 628 (s), 697 (s), 749 (m), 763 (m), 983 (vw), 1000 (vw), 1009 (s), 1028 (vw), 1038 (s), 1058 (m), 1065 (m), 1151 (m), 1160 (sh), 1211 (m), 1215 (m), 1327 (vw), 1351 (vw), 1380 (vw), 1400 (vw), 1441 (s), 1483 (m), 1599 (s), 1634 (w), 2922 (w), 2977 (w), 3036 (vw), 3100 cm$^{-1}$ (vvw). Because of a very high background apparently due to fluorescence, Raman scattering above 600 cm$^{-1}$ could not be detected. The low-frequency region is illustrated in Figure 2. The

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[24] I. R. Beattie and G. P. McQuillan, *J. Chem. Soc.*, 1519 (1963).

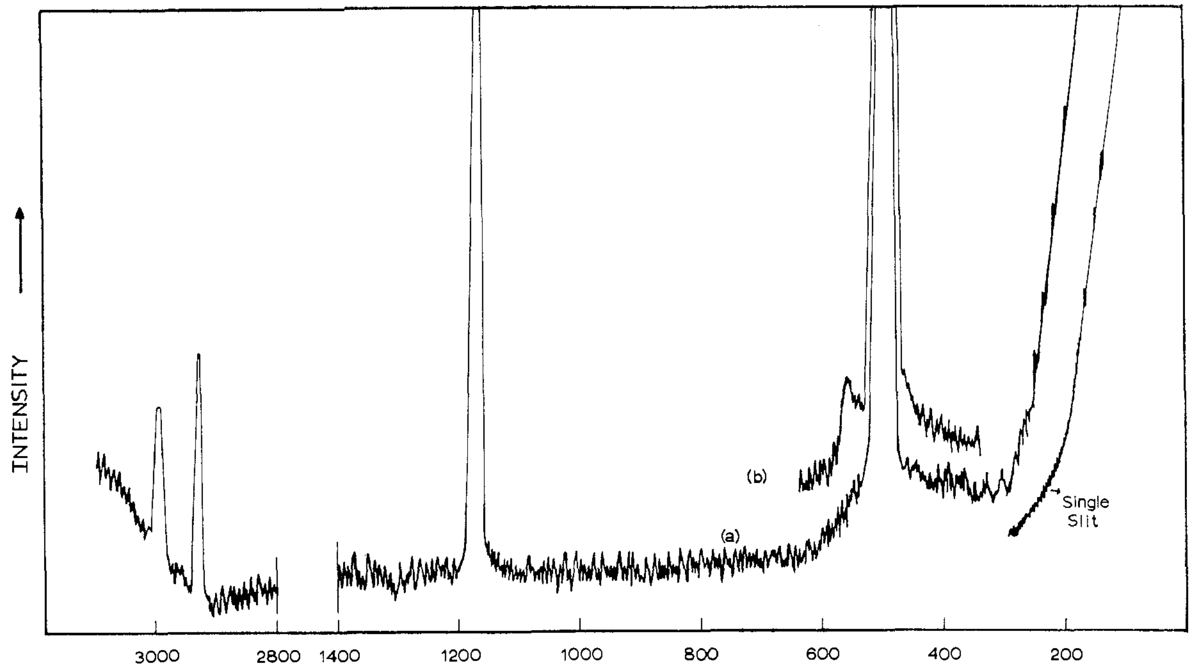

Figure 4.—Raman spectrum of an aqueous solution of $(CH_3)_2InCl$: (a) 1.2 *M;* (b) saturated.

infrared spectrum is similar to that reported by Clark and Pickard.[9]

As was the case with $(CH_3)_2Ga(acac)$, a very good Raman spectrum is obtained with $(CH_3)_2In(acac)$. The spectrum is illustrated in Figure 3. Assignments of the Raman and infrared spectra for the solid and a solution in $CCl_4$ are collected in Table II. The compound has been reported to be monomeric in benzene solution.[9] The infrared frequencies are in accord with the values of Clark and Pickard, although we have revised their assignments of the asymmetric $InC_2$ stretch on the basis of the close correspondence of the 542 (ir) and 546 $cm^{-1}$ (R) bands. The other band in each of the spectra is probably an out-of-plane acetylacetonate bending mode(s), and little is known about the nature of the mode(s).

TABLE II

INFRARED AND RAMAN FREQUENCIES AND ASSIGNMENTS FOR $(CH_3)_2In(acac)$

| $\nu$, $cm^{-1}$ | | | |
|---|---|---|---|
| | Raman | | |
| Infrared | Solid | Soln | Assignment |
| | 261 w | | |
| 413 w | 416 s | 412 s | acac out-of-plane bend and $\nu_s(InO_2)$ |
| 490 m | 495 vvs | 491 vvs | $\nu_s(InC_2)$ |
| 542 s | 546 w | 538 w | $\nu_{as}(InC_2)$ |
| 552 s | 564 w | 561 w | $\pi$-acac |
| 660 w | 664 s | 664 m | $\nu(In{-}O)$ + ring def $(A_1)$ |
| 720 vs | | | $\rho_r(In{-}CH_3)$ |
| 788 m | | | |
| 918 s | 933 m | 934 m | $\nu((C{-}CH_3)$, acac) $(A_1)$ |
| 1015 s | 1028 m | 1025 m | $\rho_r((CH_3)$, acac) |
| 1155 w | | | |
| 1162 w | 1170 s | 1168 s | $\delta_s((CH_3), In{-}CH_3)$ |
| 1200 | | | |
| 1210 w | 1216 vw | 1208 m | $\delta((C{-}H)$, acac) |
| 1248 s | 1252 vs | 1258 vs | $\nu(C\underline{\cdots}C)$ $(A_1)$ |
| 1381 vs | 1370 s | 1366 s | $\delta_s((CH_3)$, acac) |
| | 1395 s | 1398 m | |
| 1430 w | | | |
| 1449 w | 1463 vw | 1466 w | $\delta_{as}((CH_3)$, acac) |
| 1511 vs | 1517 s | 1515 s | $\nu(C\underline{\cdots}C)$ $(B_2)$ |
| 1563 w | | | |
| 1600 vs | 1608 w | 1608 w | $\nu(C\underline{\cdots}O)$ $(A_1)$ |
| 2923 w | 2925 s | 2925 s | $\nu((CH_3), InCH_3)$ |
| 2976 m | 2973 m | 2978 m | $\nu_{as}((CH_3), InCH_3)$ |
| | 3073 w | 3078 w | $\nu_s((3{-}CH)$, acac) $(A_1)$ |

Although one early report indicated that the hydrolysis of $(CH_3)_3In$ went uncontrollably with the cleavage of two In–C bonds,[25] dissolution of $[(CH_3)_2InCl]_2$ in water gives a relatively stable solution of the cation $(CH_3)_2In^+$.

The 1.2 *M* solution of $(CH_3)_2InCl$, Figure 4, exhibits only a single band in the Raman spectrum below 600 $cm^{-1}$ which is clearly assignable to $\nu_s(InC_2)$. A band at 566 $cm^{-1}$ assigned to $\nu_{as}(InC_2)$ is observed in the infrared spectrum of a thin film of the solution. When a saturated (*ca.* 5 *M*) solution is examined, a new Raman band of very low intensity appears at ~550 $cm^{-1}$ which is assigned to $\nu_{as}(InC_2)$. The intensity of this ~550-$cm^{-1}$ band relative to the symmetric stretch is much less than for the three solid compounds examined which all have angular skeletons. This behavior suggests that the $(CH_3)_2In^+$ cation has a linear skeleton in dilute solution, *i.e.*, it is isostructural with $(CH_3)_2Cd$ and $(CH_3)_2Sn^{2+}$, but that the symmetry is lowered by interaction with chloride ion in the saturated solution. The Raman spectra of these solutions are shown in Figure 4, and the spectra are tabulated in Table III.

In order to obtain a spectrum of a solution containing a noncomplexing anion, a saturated solution of $(CH_3)_2InClO_4$ was examined and the spectrum is shown in Figure 5. The frequencies are given in Table III. Again no antisymmetric $In{-}C_2$ stretch could be detected

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[25] L. M. Dennis, R. W. Work, and E. G. Rochow, *J. Amer. Chem. Soc.*, **56**, 1947 (1934).

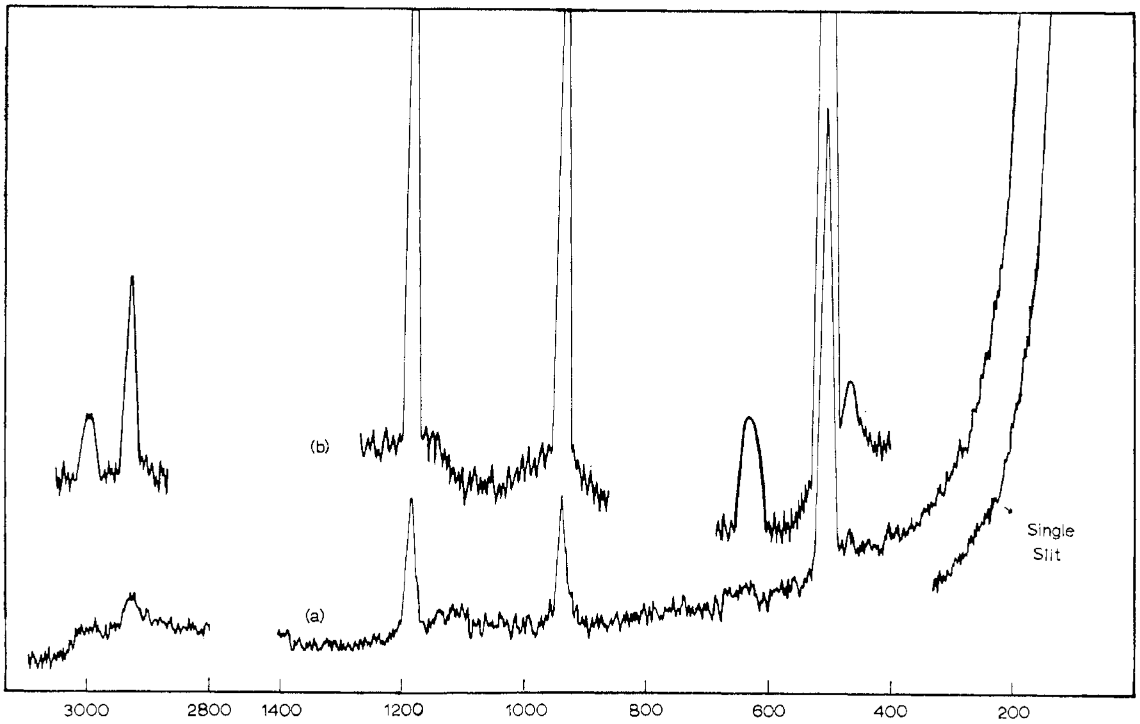

Figure 5.—Raman spectrum of a saturated aqueous solution of $(CH_3)_2InClO_4$. Sensitivity: (a) 5 × 100; (b) 3 × 1000.

TABLE III

RAMAN AND INFRARED FREQUENCIES AND QUALITATIVE ASSIGNMENTS FOR AQUEOUS SOLUTIONS CONTAINING $(CH_3)_2In^+$

| $\nu[[(CH_3)_2InCl]_2]$, cm$^{-1}$ | | | $\nu[(CH_3)_2In(ClO_4)]$, cm$^{-1}$ | |
|---|---|---|---|---|
| Raman, 1.2 *M* | Raman, satd | Ir | Raman, satd | Qualitative assignments |
| | | | 468 w | $\nu_2(ClO_4^-)$ |
| 500 vvs | 499 vvs | . . . | 502 vvs | $\nu_s(InC_2)$ |
| | 550 w | 566 m | . . . | $\nu_{as}(InC_2)$ |
| | | | 628 | $\nu_4(ClO_4^-)$ |
| | | $742^a$ m | | $\rho_r(InCH_3)$ |
| | | | 936 | $\nu_1(ClO_4^-)$ |
| | | 1176 vw | | $\delta_s(CH_3)$ |
| 1182 m | 1178 m | | 1183 m | |
| | | $2927^a$ s | | $\nu_s(CH_3)$ |
| 2929 m | 2921 m | | 2928 w | |
| 2996 w | 2993 w | | 3003 w | $\nu_{as}(CH_3)$ |
| | | $2996^a$ s | | |

[a] $D_2O$ solution.

indicating that the cation has a linear skeleton even in the concentrated perchlorate solution.

**Normal-Coordinate Analysis.**—Force constants were calculated for $(CH_3)_2In^+$ using the data from the aqueous solution spectra and assuming $D_{3d}$ effective symmetry. The same Urey–Bradley force field and procedure described earlier was used.[4] Trial values for all of the force constants were taken from the isosteric $(CH_3)_2Sn^{2+}$ ion, and $K$(C–H), $K$(C–In), $H$(H–C–H), $H$(H–C–In), and $F$(H· · ·H) were refined by the method of least squares. Since no skeletal deformation was observed, the calculation was carried out with a small, constrained value for $H$(C–In–C). Large variations in this constant have no significant effect except on the lowest frequency $e_u$ mode. The nonbonded interaction $F$(H· · ·In) was taken equal to that for $(CH_3)_2Cd$, 0.39 mdyn/Å, which is essentially the same as that for $(CH_3)_2Sn^{2+}$, 0.40 mydn/Å. The Urey–Bradley force constants and the diagonal elements of the **F** matrix in internal coordinates together with the standard errors taken from the last cycle of least-squares refinement are tabulated in Table IV, and the calculated and observed frequencies are given in Table V.

**Nmr Spectra.**—Dimethylindium chloride gives a single, sharp methyl proton resonance both in solution in organic solvents ($\tau_{CCl_4}$ 9.60, $\tau_{CHCl_3}$ 9.72 ppm, TMS =

TABLE IV

UBFF FORCE CONSTANTS[a] AND THE DIAGONAL *F* MATRIX ELEMENTS FOR $(CH_3)_2In^{+b}$

| Description | U–B | $F_{dia}$ |
|---|---|---|
| $K$(C–H) | 4.62 (0.01)[c] | 4.87 (0.01)[c] |
| $K$(C–In) | 1.36 (0.03) | 2.33 (0.03) |
| $H$(H–C–H) | 0.47 (0.01) | 0.51 (0.01) |
| $H$(H–C–In) | 0.07 (0.004) | 0.38 (0.004) |
| $H$(C–In–C) | 0.51[e] | 0.51 |
| $F$(H· · ·In) | 0.39[e] | . . . |
| $F$(H· · ·H) | 0.07 (0.01) | . . . |
| $\kappa$[d] | 0[e] | . . . |

[a] $K$ and $F$ in mdyn/Å; $H$ and $\kappa$ in mdyn Å. [b] Bond lengths used in calculation: $R$(In–C) = 2.06, $R$(C–H) = 1.093 Å. ∠H–C–H = ∠H–C–In = tetrahedral angle; ∠C–In–C = 180°. [c] Standard errors in parentheses. [d] Internal tension parameter. [e] Constrained.

TABLE V

OBSERVED AND CALCULATED FREQUENCIES for $(CH_3)_2In^{+a}$

| Symmetry species | $\nu$, cm$^{-1}$ Obsd | $\nu$, cm$^{-1}$ Calcd | Symmetry species | $\nu$, cm$^{-1}$ Obsd | $\nu$, cm$^{-1}$ Calcd |
|---|---|---|---|---|---|
| $A_{1g}$ | 2928 | 2928 | $E_g$ | 3003 | 2999 |
| | 1183 | 1180 | | *b* | 1404 |
| | 502 | 503 | | *b* | 736 |
| $A_{2u}$ | 2927 | 2928 | $E_u$ | 2996 | 3000 |
| | 1176 | 1180 | | *b* | 1404 |
| | 566 | 565 | | 742 | 743 |
| | | | | *b* | 174 |

[a] Average error 0.15%. [b] Not observed.

10) and in aqueous solution (10.05 ppm, trimethylsilyl propanesulfonate = 10). When the chloride is dissolved in 0.5 *M* HCl or $HNO_3$, decomposition occurs, probably with the formation of a monomethylindium(III) species.

Carbon-13–proton coupling constants were measured using a CAT for aqueous solutions of $(CH_3)_2InCl$, $(CH_3)_2TlClO_4$, and $(CH_3)_2Pb(ClO_4)_2$. The values were 130 ± 1 (1 *M*) (127 ± 1 saturated), 137 ± 1, and 148 ± 1 Hz, respectively. For comparison, a value of 135 Hz has been reported for solutions of $(CH_3)_2Sn(ClO_4)_2$[26] and 127, 130 Hz for neat $(CH_3)_2Cd$[27] and $(CH_3)_2Hg$,[27] respectively.

## Discussion

As is true for most of the methyl derivatives of the heavier metals, Raman spectra because of their high intensity are particularly useful for studying vibrations involving the metal–carbon bonds. For the compounds with four-coordinate indium and consequently an angular $(CH_3)_2In^{III}$ moiety, $[(CH_3)_2InCl]_2$, $(CH_3)_2InCl \cdot py$, and $(CH_3)_2In(acac)$, the symmetric $InC_2$ stretching vibration occurs in the range 489–500 $cm^{-1}$, while the asymmetric stretches are in the range 527–563 $cm^{-1}$. As predicted, $\nu_s$ and $\nu_{as}$ are active for the monomeric compounds in both the Raman and infrared spectra.

Indium-terminal chlorine stretching gives a well-defined band with $(CH_3)_2InCl \cdot py$ at 254 (Raman) and 264 $cm^{-1}$ (infrared). The poor agreement between these values is surprising, although the Raman spectrum was not of high quality because of fluorescence. The bridge chlorides of $[(CH_3)_2InCl]_2$ do not show bands in the same region, and these stretching vibrations appear to occur at significantly lower frequency. Only a low-intensity band at 193 $cm^{-1}$ was observed in the Raman spectrum.

The aquodimethylindium(III) cation in saturated $(CH_3)_2InClO_4$ solution, in contrast to the other compounds examined, show only one skeletal stretch in the Raman spectrum and one in the infrared spectrum. The asymmetric $InC_2$ stretching vibration must have much lower Raman intensity for the cation than for any of the other compounds, and it is reasonable to assume that it is completely inactive because of an increase in the C–In–C angle to 180°. Comparison of this spectrum with that for the angular $(CH_3)_2Ga^+$ ion[5] also suggests that their structures are different. It may prove to be possible to stabilize the linear $(CH_3)_2In^+$ structure in a crystal by using a ligand like fluoride. Comparison of the In–C stretching force constant with the values for the metal–carbon stretching constants of the isoelectronic $(CH_3)_2Cd$ and $(CH_3)_2Sn^{2+}$ reveals the normal increase with increasing metal nuclear charge. Consequently, the decrease from $(CH_3)_2Hg$ to $(CH_3)_2Pb^{2+}$ cannot be attributed to solvation effects alone. The variation of these force constants is illustrated in Figure 6. No error limits are given in the plot, since these are difficult to estimate. Different numbers of frequencies were used in the least-squares refinements so the standard errors do not even give reliable values. Because of the similarity of the cations, the values should be quite reliable in a relative sense. Since the molecules were studied as the neat liquids, the comparison involving them is less accurate. The absolute values of the force constants are not meaningful beyond the first decimal place. The stabilization of the metal–carbon bonds in these systems probably depends in a critical way on the metal–carbon orbital overlap. The bonds exhibiting the largest stretching force constants, Hg–C, Tl–C, and Sn–C, are those which are most inert to attack by acids and bases.

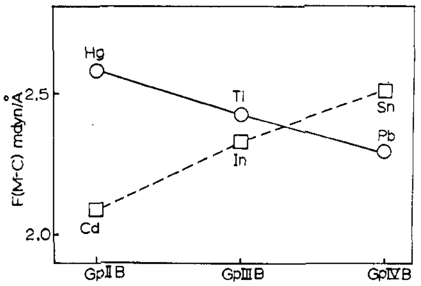

Figure 6.—Variation of the metal–carbon valence stretching force constants in isoelectronic sequences of $(CH_3)_2M$ ions and molecules.

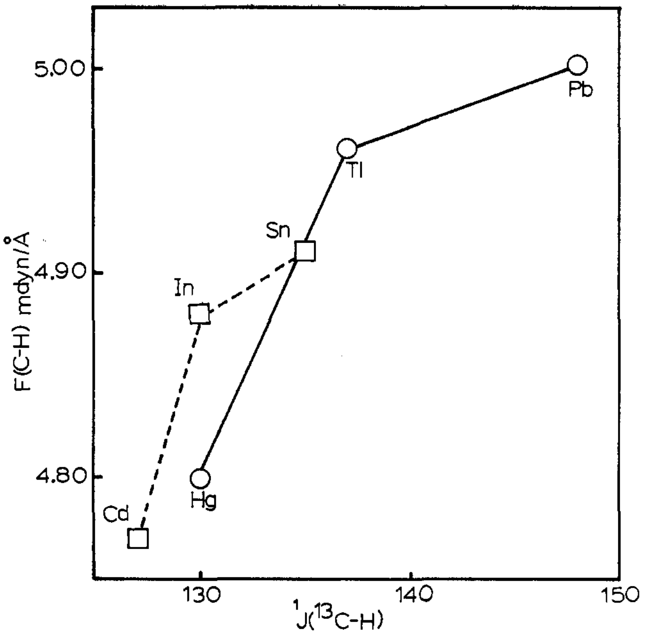

Figure 7.—Variation of the carbon-13–proton coupling constants and the carbon–hydrogen valence stretching force constants of $(CH_3)_2M$ ions and molecules.

The carbon-13–proton coupling constants for these dimethylmetal ions and molecules show significant variations. In general, it has been observed that there is a correlation between the $^1J(^{13}C\text{–}H)$ values and the carbon–hydrogen valence stretching force constants for organic molecules.[28] The changes in the coupling con-

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[27] F. J. Weigert, M. Winokur, and J. D. Roberts, *ibid.*, **90**, 1566 (1968).

[28] See T. L. Brown and J. C. Puckett, *J. Chem. Phys.*, **44**, 2238 (1965), and references therein.

stants have been attributed to rehybridization at the carbon atom,[29,30] although with a highly electronegative Y atom in $CH_3Y$, the effect of changes in the effective nuclear charge of carbon on the 2s orbital appears to make a substantial contribution.[31] The data for the six dimethylmetal ions and molecules are illustrated in Figure 7 which shows that an increase in $^1J(^{13}C–H)$ is paralleled by an increase in $K$(C–H), the valance stretching force constant. There is no obvious correlation with what would be expected for the orbital electronegativities of the metals; *e.g.*, the coupling constant is greater with lead than with tin and greater with thallium than with indium. Because the largest coupling constant within an isoelectronic sequence occurs with the dipositive cation, it seems likely that these variations may arise from contraction of the carbon 2s orbital. The charge also would tend to lead to increased ionic character in the C–H bonds, and Brown and Puckett[28] have suggested that this is the primary cause for increase in C–H stretching force constants. As a result of these factors, there is no simple correlation between the metal–carbon bond strengths and the carbon-13–proton–coupling constants or the C–H stretching force constants. The low values for the (C–H) stretching force constants for $(CH_3)_2Cd$ and $(CH_3)_2Hg$ may reflect the fact that they were measured under different conditions than the ions. The relative values for the cations are probably significant to ±0.01 mdyn/Å.

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# Stereochemistry of Octahedral Titanium(IV) Complexes. I. The Titanium Tetrachloride–Titanium Tetrafluoride–Tetrahydrofuran System[1]

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Tetrahydrofuran (THF) complexes of titanium tetrachloride and titanium tetrafluoride have been found to undergo a redistribution reaction in excess THF to produce the mixed-halogen complexes. Fluorine-19 magnetic resonance spectra obtained at −60° have been used to establish both the presence of the mixed complexes and in most cases the specific isomer(s) present for each complex. Comparison of rough equilibrium constants calculated from the nmr spectral intensities with those calculated statistically for random ordering shows that the formation of the mixed-halogen complexes is nearly a random process whereas the formation of the specific isomers for a given complex is apparently controlled by other factors. The following information was determined for each of the observed species. $TiF_4 \cdot 2THF$: Only the *cis* isomer (I) was observed, with $\delta_{FF}$ 60 ppm and $J_{FF}$ = 38 Hz. $TiClF_3 \cdot 2THF$: Only one isomer was observed with *cis* THF and *trans* fluorine groups (III), with $\delta_{FF}$ 67 ppm and $J_{FF}$ = 33 Hz. $TiCl_2F_2 \cdot 2THF$: Two isomers were observed. One contains similar ligands *cis* (X), with $\delta_{FF}$ 76 ppm and $J_{FF}$ = 45 Hz. The structure of the second isomer remains in doubt. $TiCl_3F \cdot 2THF$: The only isomer observed for this compound is believed to contain the fluorine *trans* to a chlorine (XII or XIII).

## Introduction

The stereochemistry of a number of titanium(IV) octahedral complexes has been previously examined. A number of titanium tetrafluoride complexes have been studied by low-temperature fluorine-19 magnetic resonance.[3-9] In a recent article by Dyer and Ragsdale[9] the factors responsible for the *cis* or *trans* orientation of the donor molecules for complexes of the type $TiF_4 \cdot 2$(donor) are summarized. They suggested that the *cis* isomer is favored by the tendency to maximize pπ–dπ bonding and symmetry effects and that the *trans* isomer only exists when these factors can be overcome by steric interactions (bulky donor groups). A number of dihalobis(β-diketonato)titanium(IV) complexes also have been studied by Fay, *et al.*,[10,11] and were found to contain *cis* halides. The factors responsible for the preference of *cis* halides were not discussed.

We have prepared a series of mixed-halide complexes which may provide additional insight into the nature of

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[1] Presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

[2] (a) Taken in part from the Ph.D. Thesis of Robert S. Borden, Michigan State University, 1967. (b) Wittenberg University. (c) Michigan State University.

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