tively, in that there is observed too much spectral intensity near 810 cm^{-1}. It is noteworthy that in both $As(OH)_3$ and AsO_3^{3-} the asymmetric stretching modes come at lower frequency than the symmetric modes; in $AsO(OH)_2^-$ the asymmetric stretching mode (610 cm^{-1}) is at higher frequency than the symmetric $-As(OH)_2$ stretch (570 cm^{-1}) as with C_{2v} structures in general. It is, thus, reasonable to expect that the asymmetric $-AsO_2$ mode of the $AsO_2(OH)^{2-}$ comes at a higher frequency than its symmetric $-AsO_2$ stretching mode. Carrying this reasoning one step further, we might expect the symmetric $-AsO_2$ motion to be approximately midway between the observed frequencies of $AsO(OH)_2^-$ and AsO_3^{3-} (790 and 752 cm^{-1}, respectively) or at ~770 cm^{-1}; the asymmetric mode may well fall ~40 cm^{-1} higher or near 810 cm^{-1}. Indeed, the observed spectra in this region show greater intensity than is expected if only $AsO(OH)_2^-$ and AsO_3^{3-} are present. Thus, the expected species $AsO_2(OH)^{2-}$ apparently does have a Raman spectrum at anticipated frequencies. Table IV summarizes the frequency assignments.

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Reactions of Dimethylgallium(III) Hydroxide. Raman, Infrared, and Proton Magnetic Resonance Spectra of the Dimethylgallium(III) Aquo Ion and Several of Its Compounds[1]

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Dimethylgallium(III) hydroxide reacts readily with both acids and bases without rupture of the gallium–carbon bonds. The Raman, infrared, and pmr spectra of aqueous solutions of dimethylgallium(III) nitrate and perchlorate and of sodium dihydroxodimethylgallate(III) have been measured, and they are consistent only with an angular structure for the dimethylgallium(III) moiety. The skeletal vibrational frequencies of the aquo ion are very similar to those of dimethylgallium(III) hydroxide and acetylacetonate suggesting that the labile aquo complex is $(CH_3)_2Ga(OH_2)_2^+$ analogous to the known and isoelectronic $(CH_3)_2Ga(NH_3)_2^+$. Thus in aqueous solution $(CH_3)_2Ga^{III}$ adopts a structure analogous to that of the isoelectronic $(CH_3)_2Ge^{IV}$ rather than the isoelectronic $(CH_3)_2Zn$. Pmr and Raman spectra indicate that only one molecular species of dimethylgallium(III) hydroxide exists in solutions with organic solvents. The similarity of the Raman and infrared spectra of the solid hydroxide which contains $[(CH_3)_2GaOH]_4$ molecules and the corresponding solution spectra suggests that the tetramer persists in solution. The pmr data show that the dimethylgallium hydroxide polymer is very flexible in contrast to $[(CH_3)_2AuOH]_4$ which has a somewhat similar structure and which behaves in solution as a stereochemically rigid molecule. The vibrational frequencies and intensity data indicate an increase in the C–Ga–C bond angle in the sequence $(CH_3)_2Ga(OH)_2^-$, $[(CH_3)_2GaOH]_4$, and $(CH_3)_2Ga(OH_2)_2^+$.

Introduction

By comparing a series of analogous organometallic moieties under comparable conditions as, for example, the aquo complexes in moderately dilute solutions, it is possible to study trends in the nature of the metal–carbon bonds. The use of solutions eliminates problems with low site symmetry often encountered with crystals. Metal ions with two CH_3 groups in the first coordination sphere are particularly simple systems for study. With a ligand like water, which has a rather electronegative donor atom, the heavy-metal dimethyls $(CH_3)_2Tl^+$, $(CH_3)_2Pb^{2+}$, and $(CH_3)_2Sn^{2+}$ have a linear structure similar to the isoelectronic molecules $(CH_3)_2Hg$ and $(CH_3)_2Cd$.[4] The dimethyltin(IV) moiety also exhibits an angular structure in many compounds with less electronegative ligands, and the angular → linear transition appears to be accompanied by a rather large increase in the s character of the metal orbitals used in bonding the carbon atoms.

Trends among the lighter metal alkyls have been much less thoroughly investigated. The dimethylgermanium(IV) entity which is isoelectronic with the linear molecule $(CH_3)_2Zn$ has a bent structure in aqueous solutions; however, it is completely hydrolyzed to the uncharged dihydroxide.[5]

The first aim of this investigation was to determine whether the dimethylgallium(III) moiety can exist in solution as an aquo cation and, if so, to ascertain the structure of the solute, that is, whether it is linear as the isoelectronic dimethylzinc(II) or angular as the isoelectronic dimethylgermanium(IV) moiety. Raman spectroscopy is a particularly suitable technique for this purpose. In the presence of ammonia, dimethylgallium(III) chloride forms $(CH_3)_2GaCl \cdot 2NH_3$ which has been shown to have an ionic lattice and to contain the cation $(CH_3)_2Ga(NH_3)_2^+$.[6]

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(1) Supported, in part, by the National Science Foundation, Grant GP-5022.

(2) Research Fellow in Chemistry.

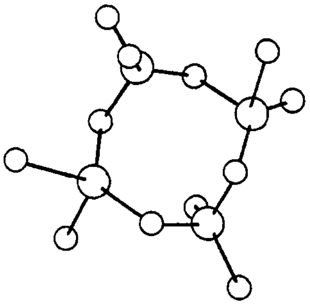
(3) NASA Trainee, 1964–1967.

(4) R. S. Tobias, *Organometal. Chem. Rev.*, **1**, 93 (1966).

(5) R. S. Tobias and S. Hutcheson, *J. Organometal. Chem.* (Amsterdam), **6**, 535 (1966).

(6) D. F. Shriver and R. W. Parry, *Inorg. Chem.*, **1**, 835 (1962).

Additionally, in order to compare the properties of dimethylgallium(III) moiety in the parent hydroxide and the species present in aqueous solution, the hydroxide was examined by Raman, infrared, and pmr spectroscopy. It was also of interest to compare the spectrum of the hydroxide in the crystalline state and in solution in organic solvents to determine if it undergoes structural changes upon dissolution. Dimethylgallium(III) hydroxide was first examined in detail by Kenney and Laubengayer, who prepared the compound by the careful hydrolysis of trimethylgallium diethyl etherate.[7] In the crystalline state, an X-ray investigation has shown that the hydroxide (I) is tetrameric with C_i symmetry and with two carbon and two oxygen atoms arranged tetrahedrally about gallium.[8] The degree of polymerization in solutions with organic solvents was not established definitely, although it appeared to be less than or equal to 4.[7,8] It was also instructive to compare the solution behavior of this tetrameric molecule with the structurally similar dimethylgold(III) hydroxide which has also been shown by an X-ray investigation to be tetrameric in crystals (II) with approximately S_4 symmetry.[9]



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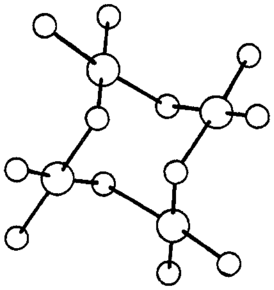

II

Dimethylgallium(III) acetylacetonate was also studied as an example of a simple monomeric compound with gallium–oxygen and gallium–carbon bonds. This compound was first prepared by reaction of $(CH_3)_3Ga$ with acetylacetone.[10]

In general dimethylgallium(III) is four-coordinate, but with fluoride ion[11] and with water[12,13] gallium(III) attains six-coordination.

Experimental Section

Dimethylgallium Hydroxide.—This compound was prepared by alkylation of $GaCl_3 \cdot O(C_2H_5)_2$ in diethyl ether with methyllithium and hydrolysis of the resulting $(CH_3)_3Ga \cdot O(C_2H_5)_2$.[14] After evaporation of the ether, the product was recrystallized repeatedly from petroleum ether (bp 30–60°); mp 86.5–87.5° dec, lit.[5] mp 87–88.5° dec. *Anal.* Calcd for C_2H_7OGa: C, 20.6; H, 6.04; Ga, 59.7. Found: C, 20.3; H, 6.11; Ga, 59.9. The mass spectrum at 60° for the ion molecules containing *only* ^{69}Ga (Hitachi Perkin-Elmer RMU-60) yielded *m/e* 433, 415, 399, 384, 333, 315, 299, 283, 269, 255 ± 1, 239 ± 1, 217, 199, 185 ± 1, 169 ± 1, 99, 84, and 69. The equivalent weight of the dimethylgallium(III) hydroxide was determined by dissolving weighed samples in standard perchloric acid giving a 4 m*M* solution. Calcd: equiv wt, 116.8. Found: equiv wt, 116.0. From a plot of $\bar{n}$, the average number of hydrogens transferred from the aquodimethylgallium(III) ion, an upper limit of 4.2×10^{-6} was estimated for the first acid dissociation constant $^*K_1$ and an upper limit of 1.5×10^{-9} for the second dissociation constant $^*K_2$, both at 25° in an ionic medium with $[ClO_4^-] = 0.3\ M$.[15]

The partially deuterated hydroxide was obtained by dissolving dimethylgallium hydroxide in a dilute solution of perchloric acid in D_2O and by precipitating the hydroxide with NaOD to yield $(CH_3)_2GaOD$.

Dimethylgallium(III) Nitrate and Perchlorate.—Solutions of $(CH_3)_2GaNO_3$ and $(CH_3)_2GaClO_4$ were prepared by dissolving weighed quantities of $(CH_3)_2GaOH$ in weighed amounts of standard nitric and perchloric acids at 0°. The hydroxide dissolves readily with no methane evolution. After standing at room temperature for several hours, very small quantities of gas were evolved. This occurred steadily over a period of several weeks giving, presumably, $(CH_3)Ga_{aq}^{2+}$ and Ga_{aq}^{3+} (hydrolyzed) as products.

Sodium Dihydroxodimethylgallate(III).—Solutions of $Na[(CH_3)_2Ga(OH)_2]$ were prepared by dissolving weighed amounts of dimethylgallium hydroxide in weighed amounts of standard sodium hydroxide at 0°. The dimethylgallium(III) hydroxide is readily soluble in an equivalent quantity of base without rupture of the gallium–carbon bonds.

Acetylacetonatodimethylgallium(III).—Dimethylgallium(III) hydroxide (3.83 g, 0.0328 mol) was dissolved in 50 ml of diethyl ether and 3.55 g (0.0354 mol) of acetylacetone was added. The cloudy liquid produced was diluted to 100 ml with ether and washed thoroughly three times with water to remove the unreacted acetylacetone. The ether solution was evaporated at low temperature to about one-fourth the original volume, repeatedly fractionated on the vacuum line, and distilled from anhydrous $CaSO_4$ to give a colorless liquid which melted in a sealed tube at 21°; lit.[10] mp 21.8–22°. *Anal.* Calcd for $C_7H_{13}GaO_2$: C, 42.3; H, 6.59; Ga, 35.0. Found: C, 42.1; H, 6.75; Ga, 35.0. For the Raman spectra, the compound was distilled into a Raman cell and sealed off.

Raman Spectra.—The Raman displacements from the 4358-Å mercury line were recorded photoelectrically with a Cary Model 81 spectrophotometer. All spectra were recorded within a few hours after preparation of the solutions. The solution samples were maintained at approximately 0° by pumping water through a jacket around the 7-mm cell. Solid samples were run in a conical cell and maintained at *ca.* −20° by blowing cold nitrogen over the cell. Integrated intensities were determined with a Gelman planimeter. Depolarization ratios were measured using large Polaroid cylinders which surrounded the water-jacketed cell, and the observed values were corrected when possible using internal standards to calculate values of the parameters α and β in the empirical expression

$$\rho = \frac{I_{\parallel} - \alpha I_{\perp}}{I_{\perp} - \beta I_{\parallel}} \qquad (1)$$

Here $I_{\parallel}$ is the integrated intensity with the axial polarizer, and $I_{\perp}$ is the intensity with the crossed polarizer in place.

With the aqueous solutions, a base line for the intensity measurements was established from spectra of water or of aqueous solutions of NaOH, $NaClO_4 + HClO_4$, or $KNO_3 + HNO_3$ of appropriate concentrations. Perchlorate ion was used as the internal standard for the aqueous solutions, and α was evaluated

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(7) M. E. Kenney and A. W. Laubengayer, *J. Am. Chem. Soc.*, **76**, 4839 (1954).

(8) G. S. Smith and J. L. Hoard, *ibid.*, **81**, 3907 (1959).

(9) G. E. Glass, J. H. Konnert, M. G. Miles, D. Britton, and R. S. Tobias, *ibid.*, **90**, 1131 (1968).

(10) G. E. Coates and R. G. Hayter, *J. Chem. Soc.*, 2519 (1953).

(11) S. Schwarzmann, *Z. Krist.*, **120**, 286 (1964).

(12) D. Fiat and R. E. Connick, *J. Am. Chem. Soc.*, **88**, 4754 (1966).

(13) T. J. Swift, O. G. Fritz, Jr., and T. A. Stephenson, *J. Chem. Phys.*, **46**, 406 (1967).

(14) M. J. Sprague, G. E. Glass, and R. S. Tobias, *Inorg. Syn.*, submitted for publication.

(15) S. J. Harris, unpublished research; the general procedures used in these experiments were similar to those employed in other recent studies in this laboratory. See, for example, C. E. Freidline and R. S. Tobias, *Inorg. Chem.*, **5**, 354 (1966).

from the intensity of ν_1 ($\rho = 0$) and β from the intensities of ν_3 or ν_4 ($\rho = {}^6/_7$). Corrections were made for the carbon tetrachloride solutions using the solvent as a standard. The values obtained for α were fairly consistent and large, while β was small in most cases and quite sensitive to small errors in the measured intensities. Typical values are listed in Table I. Intensities were measured for four different spectra and an average value was taken. The general procedures employed in these measurements have been described earlier.[16]

Table I

Parameters for Correction of Observed Depolarization Ratios

α	β	Ref
0.24	−0.03	CCl_4[a] (ν_1, ν_2) } for $[(CH_3)_2GaOH]_4$
0.24	−0.02	CCl_4 (ν_1, ν_4) }
0.19	+0.25	$(CH_3)_2GaClO_4$ (ν_1, ν_3)
0.29	−0.03	2.5 *M* $NaClO_4$, 0.5 *M* $HClO_4$ (ν_1, ν_4)
0.29	+0.05	2.5 *M* $NaClO_4$, 0.5 *M* $HClO_4$ (ν_1, ν_3)
0.24	+0.05	2 *M* $LiSO_4$ (ν_1, ν_4)
0.24	+0.21	2 *M* $LiSO_4$ (ν_1, ν_3)

[a] Internal standard.

Infrared Spectra.—The infrared spectra were recorded with a Perkin-Elmer 521 spectometer using CsI disks and windows for solid samples and KBr windows with liquid cells. A polystyrene film was used to calibrate the spectrometer. Spectra of aqueous solutions were obtained with cells having AgCl windows.

Proton Magnetic Resonance Spectra.—A Varian Associates Model A-60 spectrometer equipped with a V 6020 heat exchanger and V 6040 variable-temperature controller was used to obtain the spectra. Calibration of the field sweep was effected using the side-band method. Accurate measurements of line positions were made by bracketing the resonance of interest with side bands of the resonance line of the internal standard. The accuracy is believed to be ±0.2 cps.

Results

The Raman shifts for the aqueous solutions of dimethylgallium perchlorate and nitrate and sodium dihydroxodimethylgallate(III) are listed in Table II. Infrared data are reported in Table III. Figure 1 shows the Raman spectra of the nitrate and the sodium dihydroxodimethylgallate(III) in aqueous solution.

The coincidences between the Raman and the infrared spectra and the activity of both the symmetric and the antisymmetric skeletal stretching vibrations in both the Raman and the infrared spectra immediately indicate an angular structure for the $(CH_3)_2Ga^{III}$ moiety. The Raman shifts are easily assigned on the basis of the depolarization ratios. Coates and Mukherjee have studied the infrared spectra of several dimethylgallium compounds with tetrahedrally coordinated gallium.[17] They reported that the symmetric C–Ga–C skeletal stretch occurs in the range 533–549 cm^{-1}, the antisymmetric stretch occurs at 580–606 cm^{-1}, and the symmetric methyl deformation occurs at 1190–1203 cm^{-1}. The aquo cation frequencies are all higher than those observed by Coates and Mukherjee, while the anion frequencies fall virtually within the ranges reported by them. With the aquo cation, the Ga–O stretching vibration has an intensity too low to be observed, but it occurs in the anion spectrum at 495 cm^{-1}. The Raman line observed in the range 160–169 cm^{-1} is assigned to skeletal bending. It is probably real, since it is about three times as intense as the background scattering as determined by comparison with solvent bands. Weak lines in this region are rather difficult to distinguish from the grating ghosts.

Table II

Raman Frequencies (cm^{-1}) (Relative Intensities, Depolarization Ratios) for Aqueous Solutions of Dimethylgallium(III) Salts at 0°

2.52 *M* $[(CH_3)_2Ga]ClO_4$[a]	2.49 *M* $[(CH_3)_2Ga]NO_3$[b]	2.42 *M* Na-$[(CH_3)_2Ga(OH)_2]$[c]	Assignment
2982 (40, 0.89)	2984 (42, 0.85)	2959 (71, 0.75)	$\nu_{as}CH_3$
2918 (72, 0.059)	2919 (83, 0.16)	2918 (48, 2885 (61, 0.08)	ν_sCH_3
1218 (25, 0.42)	1218 (25, 0.57)	1197 (46, 0.44)	δ_sCH_3
...	...	675 (4, –)	
d	620 (8, 1.07)	574 (24, 0.89)	$\nu_{as}GaC_2$
557 (100, 0.09)	558 (100, 0.40)	539 (100, 0.15)	ν_sGaC_2
...	...	495 (24, –)	νGaO_2
165 (31, 1.54)	160 (30, 1.21)	169 (53, –)	δGaC_2

[a] Solution is 0.58 *M* in $HClO_4$; perchlorate lines are observed at 1120 (ν_3), 936 (ν_1), 626 (ν_4), and 467 (ν_2) cm^{-1}. Depolarization ratios were corrected using the perchlorate ion as an internal standard. [b] Solution is 0.64 *M* in HNO_3; nitrate lines are observed at 1435 (ν_3), 1051 (ν_1), and 722 (ν_4) cm^{-1}. Depolarization ratios were uncorrected. [c] Solution is 0.077 *M* in NaOH; depolarization ratios were corrected using $NaClO_4$ as an internal standard; background was subtracted using data for NaOH solutions. [d] Obscured by the 626-cm^{-1} (ν_4) perchlorate line.

Table III

Infrared Spectra of Aqueous Solutions of Dimethylgallium(III) Perchlorate and Nitrate (cm^{-1})

$[(CH_3)_2Ga]ClO_4$[a]	$[(CH_3)_2Ga]NO_3$[b]	Assignment
2977,[c] 2979	2973[c]	$\nu_{as}CH_3$
2913,[c] 2918	2913	ν_sCH_3
1217	1213	δ_sCH_3
755 vb	740 vb	ρ_rCH_3
...	618	$\nu_{as}GaC_2$
554,[c] 557	552	ν_sGaC_2

[a] A perchlorate band is observed at 626 cm^{-1} which obscures the cation band at *ca.* 618 cm^{-1}. [b] Nitrate bands are observed in the range 1305–1490 cm^{-1}. [c] D_2O solutions.

Raman and Infrared Spectra of $[(CH_3)_2GaOH]_4$ and $(CH_3)_2Ga(acac)$.—The spectra of dimethylgallium hydroxide recorded with both solid and solution samples are given in Table IV, and the solid spectra are illustrated in Figure 2. The infrared spectrum was recorded by Kenney and Laubengayer, but no frequencies were reported nor were assignments made.

The vibrational frequencies of dimethylgallium(III) hydroxide are similar to those of $(CH_3)_2Ga(OH)_2^-$. The strong infrared bands at 1013 and 1033 cm^{-1} for the solid which decrease upon dissolution to *ca.* 970 cm^{-1} are assigned to O–H deformation vibrations of bridging hydroxide although they are unusually intense. These bands do not appear in the spectrum of $[(CH_3)_2GaOD]_4$, and a new intense band is observed for this compound at *ca.* 730 cm^{-1}. It is not possible to give accurate frequency values, since this is superimposed upon the broad methyl rocking band. These frequen-

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(16) M. G. Miles, G. E. Glass, and R. S. Tobias, *J. Am. Chem. Soc.*, **88**, 5738 (1966).

(17) G. E. Coates and R. N. Mukherjee, *J. Chem. Soc.*, **1295** (1964).

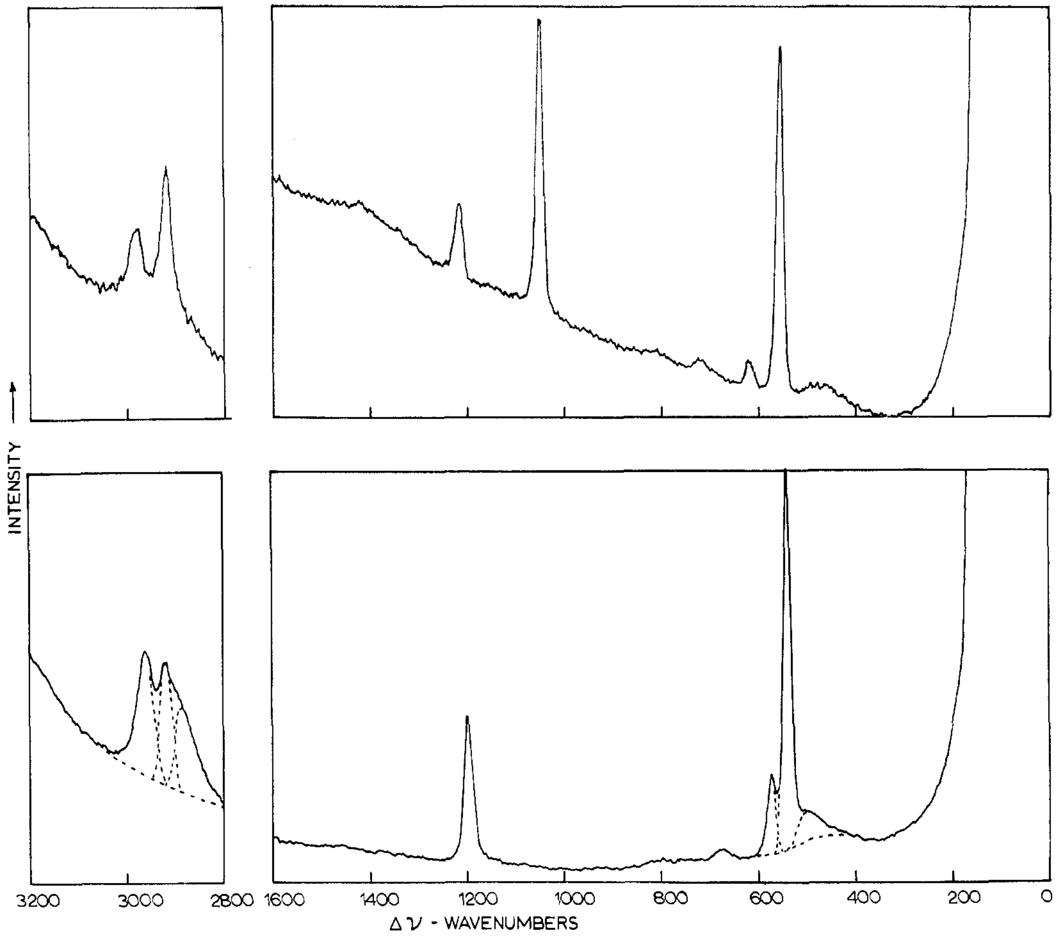

Figure 1.—Raman spectra of dimethylgallium(III) species in aqueous solutions: top, $(CH_3)_2GaNO_3$; bottom, $Na[(CH_3)_2Ga(OH)_2]$. Recorded with double slits.

TABLE IV
RAMAN AND INFRARED SPECTRA OF DIMETHYLGALLIUM HYDROXIDE (cm^{-1})

		Infrared, solid[e]		Infrared, soln		
Raman, solid[a,c]	Raman, CCl_4 soln[b,d]	$[(CH_3)_2GaOH]_4$	$[(CH_3)_3GaOD]_4$	CCl_4	CS_2	Assignment
3598 (26)	3644 (17, 0.86)	3601 s	2656 s	3643 s	3627 s	νOH
2970 (22)	2963 (51, 1.17)	2961 m	2955 m	2960 m	2959 s	$\nu_{as}CH_3$
2905 (76)	2919 2901 (119, 0.35)	2905 m	2895 m	2907 m	2904 m	ν_sCH_3
1212 (14)	1214 (33, 0.33)	1205 s	1206 s	1208 s	1206 s	δ_sCH_3
1194 (22)		1197 s	1197 s			
		1033 s	. . .			δOH
		1013 s	730 s			
				974 s, b	970 s, b	
		783 sh	785 s	*f*	*f*	ρ_rCH_3
		761 sh	760 sh	*f*	*f*	
		744 s	*h*	*f*	735 s	
		708 sh	700 sh	700 sh	696 m	
596 (18)	594 (19, 0.57)	592 s	590 s	596 s	595 s	$\nu_{as}GaC_2$
549 (100)	551 (100, 0.132)	562 s	560 s	556 m	556 s	ν_sGaC_2
		533 vs	510 vs	525 vs	524 vs	νGaOGa ring modes
396 (11)		385 sh	387 m			
		369 s	360 m		*g*	
		355 sh	. . .			
167 (107)						

[a] Values in parentheses are relative intensities. [b] Values in parentheses are relative intensities, and depolarization ratios, respectively. [c] Temperature *ca.* −20°. [d] Temperature 0°; depolarization ratios corrected using solvent as an internal standard. [e] CsI disk. [f] Obscured by solvent. [g] Not examined. [h] Obscured by OH deformation.

cies are not observed in the Raman spectra where they would be expected to have low intensity.

In order to obtain the vibrational frequencies in both the Raman and infrared spectra for a compound in which the dimethylgallium moiety occurs with two coordinated oxygens, the acetylacetonate was examined. The frequencies are reported in Table V, and the spectra are illustrated in Figure 3. The ligand vi-

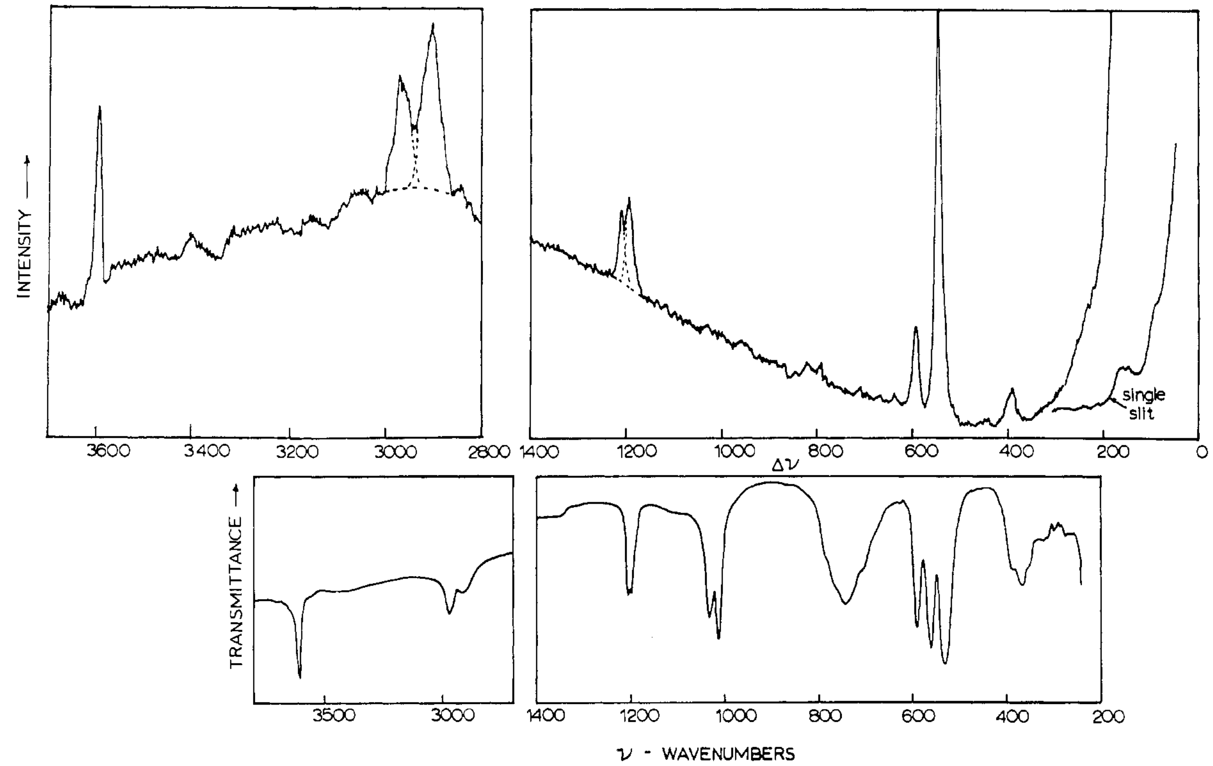

Figure 2.—Spectra of crystalline $[(CH_3)_2GaOH]_4$: top, Raman, single and double slits; bottom, infrared.

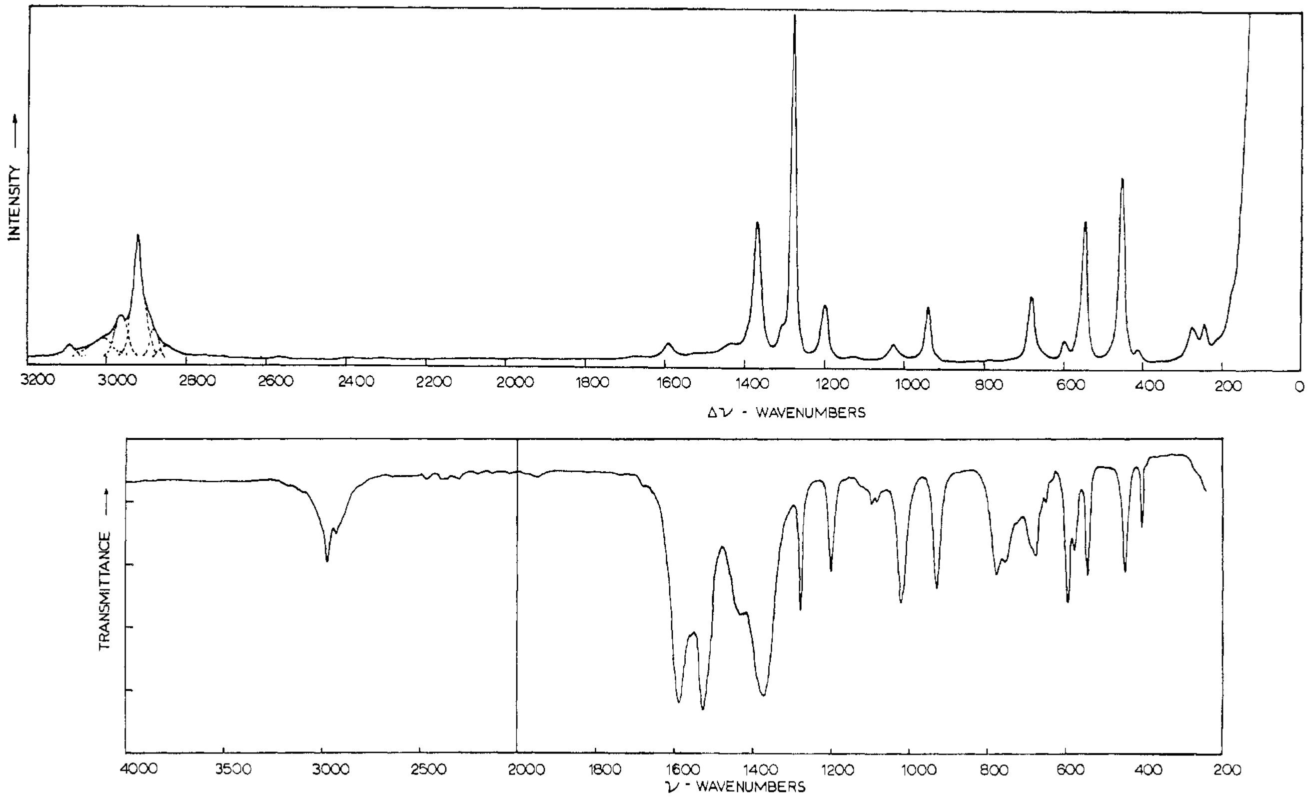

Figure 3.—Spectra of $(CH_3)_2Ga(acac)$: top, Raman double slits; bottom, infrared.

brations are assigned on the basis of the recent normal-coordinate analysis of Behnke and Nakamoto.[18] The ligand frequencies and intensities are very similar to those reported for $(CH_3)_2Sn(acac)_2$[19] and also for $Ga(acac)_3$.[20] The frequency assigned to symmetric Ga–O stretching in the spectrum of $(CH_3)_2Ga(acac)$ is only 6 cm^{-1} lower than that of $Ga(acac)_3$. It is of interest that the polarization data are in agreement with the recent revised assignments of the $C\overset{\cdots}{-}O$ (A_1) and the $C\overset{\cdots}{-}C$

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[18] G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, **6**, 433 (1967).

[19] M. M. McGrady and R. S. Tobias, *J. Am. Chem. Soc.*, **87**, 1909 (1965).

[20] R. E. Hester and R. A. Plane, *Inorg. Chem.*, **3**, 573 (1964).

TABLE V

INFRARED AND RAMAN SPECTRA OF DIMETHYLGALLIUM ACETYLACETONATE

$\Delta\bar{\nu}$ (Raman),[a] cm^{-1}	$\bar{\nu}$ (infrared), cm^{-1}	Assignment
3095 (6, 0.76)		ν_sCH (acac) A$_1$
3008 sh (12, 0.94)	3000 sh, m	ν_{as}
2966 (22, 0.89)	2964 m	ν_{as}CH$_3$ (GaCH$_3$)
2925 (67, 0.42)	2921 m	ν_sCH$_3$ (GaCH$_3$)
2843 (5, –)		
1591 (7, 0.67)	1589 s	$\nu\mathrm{C}\overset{\cdots}{-}\mathrm{O}$ A$_1$
1526 (1, –)	1528 s	$\nu\mathrm{C}\overset{\cdots}{-}\mathrm{C}$ B$_2$
1433 (10, 0.90)	1435 ms	δ_{as}CH$_3$ (acac)
1371 (66, 0.73)	1374 s	δ_sCH$_3$ (acac)
1308 (11, 0.67)		
1281 (100, 0.66)	1280 s	νC—C (acac) A$_1$
1202 (23, –)	1202 m	δ_sCH$_3$ (GaCH$_3$)
1197	1196 m, sh	δCH (acac)
1026 (9, 0.72)	1023 m	ρ_rCH$_3$ (acac)
940 (20, 0.48)	933 m	νC–CH$_3$ (acac) A$_1$
	779 m	ρ_rGa–CH$_3$
	757 m	
681 (28, 0.71)	689 m	ν(GaO + ring def) A$_1$
	681	
597 (8, 1.04)	600 m	ν_{as}GaC$_2$
561 (11, 0.93)	580 m	π acac
546 (40, 0.52)	547 m	ν_sGaC$_2$
454 (62, 0.55)	453 m	ν_sGaO$_2$
411 (5, 0.94)	411 m	acac out-of-plane bend
275 (11, ~1)		
244 (8, ~1)	240 m	

[a] Relative intensities and depolarization ratios, respectively, are given within parentheses.

(B_2) normal modes.[18] The vibrational frequencies of the dimethylgallium(III) moiety are also very similar to those in $(CH_3)_2Ga(OH)_2^-$.

Proton Magnetic Resonance Spectra.—Aqueous solutions containing dimethylgallium nitrate or perchlorate show a single methyl proton resonance at τ *ca.* 10.2 ppm. The acidic solutions decomposed slowly over several days at room temperature giving a new signal at τ 9.95 ppm which is assigned to monomethylgallium(III) species. The pmr data are tabulated in Table VI.

TABLE VI

PROTON MAGNETIC RESONANCE DATA FOR AQUEOUS SOLUTIONS OF DIMETHYLGALLIUM(III) SALTS AT 30°

Compound	[Compound], M	Solvent	τ(GaCH$_3$),[a] ppm	J^{13}(C–H), cps
$(CH_3)_2GaClO_4$	2.52	0.58 M HClO$_4$	10.19	123.6
$(CH_3)_2GaNO_3$	2.49	0.64 M HNO$_3$	10.19	123.6
$(CH_3)_2GaNO_3$	2.40	0.57 M HNO$_3$ + 4.96 M NaNO$_3$	10.18	123.8
Na[$(CH_3)_2Ga(OH)_2$]	2.42	0.08 M NaOH	10.65	118.9
Na[$(CH_3)_2Ga(OH)_2$]	1.44	2.94 M NaOH	10.65	119.0

[a] τ(trimethylsilylpropane sulfonate) 10.00 ppm.

Proton magnetic resonance data for dimethylgallium hydroxide dissolved in several organic solvents are listed in Table VII. No resolution of more than one methyl resonance was achieved even at temperatures as low as −81° in CH_2Cl_2 solution, although a slight broadening compared to the internal TMS reference was observed as the temperature was lowered. At 30°, the full width at half-intensity was 0.43 cps in CH_2Cl_2, while at −81° it was 1.07 cps. The corresponding values for TMS were 0.30 and 0.48. The width of the O–H resonance remained essentially constant at 0.9 cps.

TABLE VII

PROTON MAGNETIC RESONANCE DATA FOR DIMETHYLGALLIUM HYDROXIDE

Solvent	τ(Ga–OH), ppm[c]	τ(Ga–CH$_3$), ppm[c]
C_6H_6[a]	9.30	10.30
$CHCl_3$[a]	8.59	10.33
CH_2Cl_2[b]	8.42	10.34
CCl_4[b]	8.75	10.36
CS_2[b]	8.73	10.36

[a] 35°. [b] 30°. [c] τ(TMS) 10 ppm.

In chloroform solution the compound began to decompose within 1 hr at 70° with gas evolution. As the signal for dimethylgallium hydroxide decreased in intensity, a new signal grew in at τ 9.78 ppm until the dimethyl signal had decreased to approximately half of the initial intensity after which time both signals decreased. The ratio of the integral of the 9.30-ppm signal to that of the 10.30-ppm signal of the freshly prepared solution was 1:6.8 rather than 1:6 as expected. The carbon-13 proton coupling constants were essentially invariant at 122 ± 1 cps.

Discussion

Dimethylgallium hydroxide dissolves readily in both acids and strong bases without cleavage of the gallium–carbon bonds. The dimethylgallium(III) moiety is only weakly acidic (upper limit to the first acid dissociation constant $\sim 4 \times 10^{-6}$ M) and consequently it exists in weakly acidic aqueous solutions as a unipositive cation. The Raman spectrum of the aquo cation is only consistent with a bent structure for the dimethylgallium skeleton. It is, therefore, similar in structure to the isoelectronic $(CH_3)_2Ge^{IV}$ moiety rather than to the isoelectronic $(CH_3)_2Zn$ or the related ion $(CH_3)_2Tl^+$. There is no evidence for complexing of the aquo ion by either nitrate or perchlorate.

The similarity of the spectra of the aquo cation to those of the hydroxide, the anion $(CH_3)_2Ga(OH)_2^-$, and the acetylacetonate indicates that there are probably two water molecules coordinated by very polar bonds in the cation. The coordinated water molecules exchange with the bulk solvent very rapidly, however, and only a single averaged signal is observed in oxygen-17 resonance spectra of the solutions.[21] This is in marked contrast to the simple aquogallium(III) ion which exchanges much more slowly.[12,13,21] The structure of the aquo cation is probably very similar to that of the isoelectronic cation $(CH_3)_2Ga(NH_3)_2^+$.[6]

Several factors point to a decrease in the strength of the Ga–C bonds and the magnitude of the C–Ga–C angle as protons are removed from the coordinated water molecules to form the anion $(CH_3)_2Ga(OH)_2^-$. First, the skeletal stretching frequencies decrease from cation to anion with no further decrease as excess NaOH is added to a solution of pure Na$^+$[$(CH_3)_2Ga(OH)_2$]$^-$. Second, there is a decrease in the difference between the antisymmetric and symmetric skeletal

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(21) G. E. Glass, Ph.D. Thesis, University of Minnesota, 1967.

stretching frequencies. This would be a logical consequence of a decrease in the C–Ga–C angle[22] and is somewhat analogous to what is observed with siloxanes.[23] The low intensity of the antisymmetric stretch in the Raman spectrum of the cation compared to that of the anion also suggests a rather large C–Ga–C angle and consequently rather small derived polarizability tensor components for this normal mode.

The smaller carbon-13 proton coupling constant and the lower C–H stretching frequencies of the anion compared to the cation reflect a decrease in the effective electronegativity of the gallium atom caused by the change from coordinated water to coordinated hydroxo groups.

The factors leading to an angular structure for the dimethylgallium(III) aquo ion and a linear structure for the dimethylthallium(III) ion are of interest. Similar effects are well known in the chemistry of the group IIb elements where, with the heaviest element mercury(II), linear complexes with two bound ligands are formed. Although the metal–carbon bonds are quite stable and inert to substitution with both the gallium and the thallium ions, the gallium–oxygen bonds involve considerably more electron sharing than the thallium–oxygen bonds. The stretching of Ga–O bonds in alkaline solutions of dimethylgallium(III) gives appreciable Raman intensity, while the analogous stretching vibration of dimethylthallium(III) hydroxide solutions gives no measurable Raman scattering.[24] A large s–p separation would tend to favor a linear structure for the organometallic moiety. With gallium and thallium, this does not appear to be the answer, since the promotion energies[25] for $d^{10}s \rightarrow d^{10}p$ are 65,167 cm^{-1} for Ga^{2+} and 64,157 cm^{-1} for Tl^{2+}.

It is possible that the lower energy of the lowest d^9s state above the ground state for Tl(III), 75,052 cm^{-1}, compared to that for Ga(III), 149,298 cm^{-1}, may lead to the stability of the linear dimethylthallium(III) moiety as has been suggested for mercury(II) complexes.[26]

There is very little change in the vibrational spectrum of the tetrameric hydroxide in the solid and in solution. Unfortunately, the lower frequency Ga–O–Ga ring modes are obscured by solvent vibrations in the solution spectra. The infrared band assigned to a ring mode which occurs at 533 cm^{-1} in the solid only shifts to 525 cm^{-1} in solution indicating that little structural change occurs. If a mixture of species, *e.g.*, three- and four-membered rings, existed in solution, this also should be observable in the symmetric Ga–C_2 stretching region of the Raman spectrum, since this scattering is very intense and has a narrow line width. It is noteworthy that only one sharp line is observed.

The pmr spectra also show a single, sharp signal assigned to methyl protons of the hydroxide and one signal for hydroxo protons even at temperatures as low as −81°. If a mixture of two or more different hydroxide polymers existed in solution, the interconversion would have to occur quite rapidly to average these resonances. For comparison, solutions containing both $[(CH_3)_2GeO]_3$ and $[(CH_3)_2GeO]_4$ still show two methyl proton resonances separated by 0.023 ppm at 103° and almost 2 hr is required for equilibration of mixtures at 35°.[27] On the other hand, the Ge–O bonds are considerably stronger than the Ga–O bonds, so the interconversions would be expected to be slower with the germanium structures.

The vibrational spectra and the pmr spectra both indicate that a single dimethylgallium hydroxide molecule exists in solution. Since no changes with time are noted, it seems very likely that the molecular structure is essentially the same as in the crystal. The original studies on the hydroxide indicated approximately a trimer; however, it is difficult to measure accurately the molecular weights of such solutes, and the dipole moment values which suggest a noncentric structure were made at only one temperature.[7]

Dimethylgallium(III) hydroxide has an appreciable vapor pressure which gives rise to a very characteristic odor; however, purification by sublimation was difficult as noted by Kenney and Laubengayer[7] with a large percentage of the solid decomposing. In the mass spectrum, there are no lines assignable to a molecular ion such as $[(CH_3)_2GaOH]_4^+$, although four fragments containing four gallium atoms were observed. Molecular ions with masses corresponding to $Ga_4(CH_3)_6(OH)_4^{2+}$, $Ga_3(CH_3)_6(OH)_2^+$, $Ga_2(CH_3)_3(OH)_2^+$, and $Ga(CH_3)_2^+$ occurred with appreciable intensity.

The frequencies of the C_2Ga skeleton of hydroxide are intermediate between those of the cation and the anion probably reflecting the fact that the bridging hydroxide is intermediate between an aquo and a hydroxo group in donor strength. The C–Ga–C angle in the solid hydroxide $[(CH_3)_2GaOH]_4$ is 130°,[8] and hence it is likely that the angle is even larger than this in the aquo cation. The splitting of the symmetric methyl stretching line in the Raman spectrum of the hydroxide and of the anion is also probably a consequence of a decrease in the C–Ga–C valence angle. These are assigned to in-phase and out-of-phase vibrations of the two methyl groups, and in the limit of a linear skeleton only one is allowed in the Raman effect.

The hydroxide molecule appears to be very flexible. In the crystal it has C_i symmetry and consequently four sets of nonequivalent methyl groups and two sets of hydroxo protons. It is likely, however, that these nonequivalent protons on the same ring will exhibit small chemical shifts from one another as is the case with

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(22) This follows from the relation between the stretching frequencies and valence angle for the simple XY_2 structure. More detailed normal-coordinate analyses for similar aquo ions indicate minimal coupling between the methyl and skeletal vibrations: M. G. Miles, J. H. Patterson, C. W. Hobbs, M. J. Hopper, J. Overend, and R. S. Tobias, *Inorg. Chem.* **7**, 1721 (1968).

(23) H. Kriegsmann, *Z. Anorg. Allgem. Chem.*, **298**, 223 (1959).

(24) P. L. Goggin and L. A. Woodward, *Trans. Faraday Soc.*, **56**, 1591 (1960).

(25) C. E. Moore, "Atomic Energy Levels," National Bureau of Standards Circular 467, Vol. 2 and 3, U. S. Government Printing Office, Washington, D. C., 1952.

(26) L. E. Orgel, "Transition Metal Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1960, p 67.

(27) K. Moedritzer, *J. Organometal. Chem.* (Amsterdam), **5**, 254 (1966).

hydrocarbons[28] making it difficult to resolve the different signals except at low temperatures.

The flexibility of the dimethylgallium(III) hydroxide tetramer is much greater than that of the dimethylgold(III) hydroxide tetramer. The gold compound still shows two equal-intensity methyl proton resonances up to above 100°, while the analogous dimethylgallium hydroxide shows only a single methyl proton resonance at temperatures as low as −81°.

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(28) F. A. L. Anet and J. S. Hartman, *J. Am. Chem. Soc.*, **85**, 1204 (1963).

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Raman and Infrared Spectra of Isosteric Diammine and Dimethyl Complexes of Heavy Metals. Normal-Coordinate Analysis of $(X_3Y)_2Z$ Ions and Molecules[1]

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Raman and infrared spectra have been measured for $(H_3N)_2Ag^+$ and $(H_3N)_2Hg^{2+}$. For comparison with the aqueous solution spectra, the Raman spectrum of aqueous ammonia was also studied. Although the metal–nitrogen skeletal stretching vibrations give intense Raman scattering, the lines are very broad. Also in contrast to the analogous scattering by the isoelectronic "methido" complexes, this Raman scattering measured with aqueous solutions is only very weakly polarized. This is probably a result of the strong hydrogen bonding between the ammine groups and the solvent cage. A normal-coordinate analysis of these two ammine complexes and the isostructural dimethyl derivatives $(H_3C)_2Cd$, $(H_3C)_2Sn^{2+}$, $(H_3C)_2Hg$, $(H_3C)_2Tl^+$, and $(H_3C)_2Pb^{2+}$ has been made, including all of the ligand atoms, in order to describe the nature of the normal modes and to permit comparisons along isoelectronic sequences. Variations in the force constants are discussed. In addition, calculations were made for the isostructural $(F_3C)_2Hg$ in an attempt to ascertain the effect on the carbon–mercury bond of altering the effective electronegativity of the carbon atom.

Introduction

During the past few years, there have been many reports of syntheses of compounds containing organometallic moieties such as $(H_3C)_2In^{III}$, $(H_3C)_2Tl^{III}$, $(H_3C)_2Sn^{IV}$, and $(H_3C)_2Pb^{IV}$. Much of this work has been reviewed recently.[3-5]

In many instances, infrared and to a lesser extent Raman spectra have been used to ascertain the structure of the organometallic moiety and consequently often that of the entire complex. To assist in such work, we decided to carry out a vibrational analysis of several of these organometallic moieties together with two isoelectronic and isostructural ammine complexes for comparison. In addition, because the methyl derivatives generally yield much better Raman and infrared spectra than metal ammines, they are of value in answering some, as yet, unresolved questions about the skeletal vibrations of heavy-metal ammine complexes.

Raman and infrared spectra have been obtained previously for several "methido" complexes of metals, *i.e.*, the methyl derivatives. The dimethyl derivatives which have been studied and which are isoelectronic and isostructural with well-known metal ammine complexes include $(CH_3)_2Cd$ for which Raman (R)[6] and infrared (ir)[7] spectra have been reported; $(H_3C)_2Hg$ (R),[8] (ir);[8,9] $(H_3C)_2Tl^+$ (R);[10] $[(H_3C)_2Sn]^{2+}$ (R, ir);[11] and $[(H_3C)_2Pb]^{2+}$ (R).[12] An additional molecule of this same structural type for which both Raman and infrared data have been reported is $(F_3C)_2Hg$.[13]

The good quality of the spectra of these "organometallic" complexes even with cations such as $(CH_3)_2Pb^{2+}$ for which spectra must be obtained with crystals or aqueous solutions is a consequence of the absence of strong hydrogen bonding which broadens and distorts the spectra of metal ammines.

The infrared spectra of metal ammine complexes have been investigated by many authors,[14] and normal-coordinate calculations have been carried out for several transition metal hexaammines,[14,15] $[(H_3N)_2Hg]^{2+}$,[14] tetraammineplatinum(II),[16] and some diammineplatinum(II) complexes.[17]

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(3) K. Yasuda and R. Okawara, *Organometal. Chem. Rev.*, **2**, 255 (1967).

(4) R. S. Tobias, *ibid.*, **1**, 93 (1966).

(5) R. C. Poller, *J. Organometal. Chem.* (Amsterdam), **3**, 321 (1965).

(6) F. Feher, W. Kolb, and L. Leverenz, *Z. Naturforsch.*, **2a**, 454 (1947).

(7) H. S. Gutowsky, *J. Am. Chem. Soc.*, **71**, 3154 (1949).

(8) H. S. Gutowsky, *J. Chem. Phys.*, **17**, 128 (1949).

(9) L. A. Woodward, *Spectrochim. Acta*, **19**, 1963 (1963).

(10) P. L. Goggin and L. A. Woodward, *Trans. Faraday Soc.*, **56**, 1591 (1960).

(11) M. M. McGrady and R. S. Tobias, *Inorg. Chem.*, **3**, 1157 (1964).

(12) C. E. Freidline and R. S. Tobias, *ibid.*, **5**, 354 (1966).

(13) A. J. Downs, *J. Chem. Soc.*, 5237 (1963).

(14) The literature is reviewed by I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **22**, 759 (1966).

(15) J. M. Terrasse, H. Poulet, and J. P. Mathieu, *ibid.*, **20**, 305 (1964).

(16) H. Poulet, P. Delorme, and J. P. Mathieu, *ibid.*, **20**, 1855 (1964).

(17) K. Nakamoto, P. J. McCarthy, J. Fujita, R. A. Condrate, and G. T. Behnke, *Inorg. Chem.*, **4**, 36 (1965).