[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Polymeric Dimethylgallium Hydroxide[1] and its Condensation

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Dimethylgallium hydroxide has been prepared by the controlled hydrolysis of trimethylgallium diethyletherate and has been characterized in detail. Unlike the organo monohydroxy compounds of silicon and boron, it undergoes addition polymerization without loss of water and when heated it condenses by the elimination of methane. A tentative cyclic structure is postulated for the trimeric hydroxide on the basis of its behavior. When methane is evolved by the thermal decomposition of the hydroxide there remains a glassy, inert residue which apparently is a highly polymeric methylgallium oxide.

The condensation polymerization of the silanols, germanols and organo-substituted boric acids to oxygen-bridged systems has been widely investigated. Because some of the resulting polymers have been shown to possess such unique properties, it is important to determine to what extent corresponding ol compounds and oxygen-bridged polymers can be made for neighboring elements in the periodic table.

Previous investigators[4] had presented substantial evidence for the formation of organo hydroxides of gallium and it seemed desirable to study one of these in detail. We chose dimethylgallium hydroxide, $(CH_3)_2GaOH$), because it is the simplest member of the series and because the interesting reactions of the gallium–oxygen part of the system are not obscured by the small stable methyl groups.

Experimental

Preparation and Analysis of Dimethylgallium Hydroxide.—The diethyletherate of trimethylgallium, prepared by the method of Kraus and Toonder,[4d] was hydrolyzed in small amounts by distilling it in a vacuum line onto water which was present in slight excess and which was held frozen in a reaction tube by liquid nitrogen. The reaction mixture was allowed to warm until the hydrolysis was proceeding slowly and then the rate of the reaction was regulated by controlling the temperature. The over-all reaction apparently goes quantitatively according to the equation

$$(C_2H_5)_2O{:}Ga(CH_3)_3 + H_2O \longrightarrow (CH_3)_2GaOH + CH_4 + (C_2H_5)_2O$$

with little tendency for the hydrolytic removal of more than one methyl group. The methane and ether liberated were pumped off during the course of the reaction to avoid excessive pressure, and finally the remaining methane and ether were removed by prolonged pumping at 25°. The hydrolysate obtained is a white solid which does not react appreciably with air at room temperature, so it may be handled and stored in air without serious decomposition. Solutions of the hydroxide in organic solvents apparently undergo very slow decomposition in air. The hydroxide can be purified by cautious vacuum sublimation, but pure well-formed colorless crystals are best obtained by recrystallization from cyclohexane solutions which have not been heated above 65°.

The compound was analyzed for gallium by conversion to Ga_2O_3.[5] Carbon and hydrogen were determined by the conventional microanalytical technique. An attempt was made to determine the hydroxyl content by titration with 0.1 *M* HCl, but the break in the titration curve was not sharp enough for analytical purposes, although it did occur in the correct region. In one experiment the break in the curve occurred at a *p*H of about 3.4, as measured by a glass electrode when 96.6 mg. of the hydroxide was titrated to an end-point volume of about 30 ml. Titration with $HClO_4$ in anhydrous acetic acid was not effective. Quantitative determination of the OH group was successfully accomplished by means of the Karl Fischer reagent.[6]

Anal. Calcd. for $(CH_3)_2GaOH$: Ga, 59.7; C, 20.57; H, 6.04; OH, 14.6. Found: Ga, 59.8, 59.9; C, 19.43, 19.66; H, 5.85, 6.02; OH, 14.5, 14.5.

Infrared Spectra.—Infrared absorption spectra of cyclohexane and carbon tetrachloride solutions and of a Nujol mull of the hydroxide were obtained in the 2 to 15 μ region and are given in Fig. 1. The strong narrow absorption peak at about 2.8 μ which is common to all three spectra may be attributed to the presence of the OH bond, thus giving confirmatory evidence as to the nature of the compound.

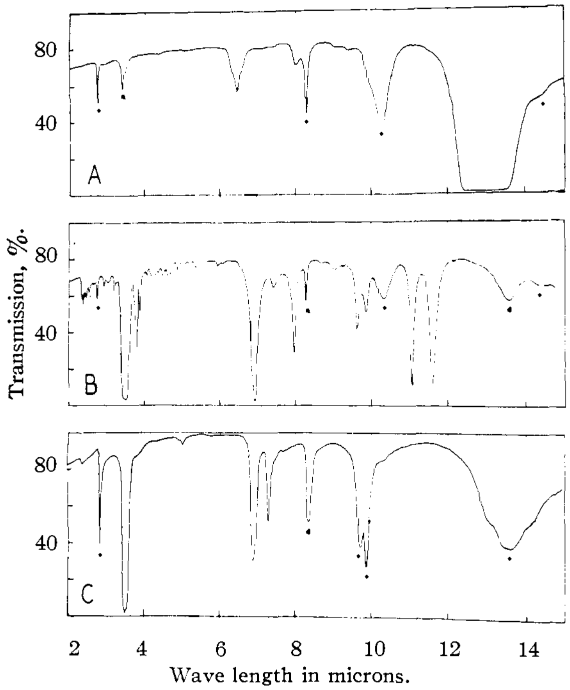

Fig. 1.—Infrared spectra of $(CH_3)_2GaOH$ in CCl_4 (A), cyclohexane (B), and in a Nujol mull (C). Features due to hydroxide indicated by dots.

Molecular Weight.—Cryoscopic measurements were made on benzene solutions in a glass vacuum-type freezing point cell. Solutions containing 18.7, 15.6 and 10.6 g. of hydroxide per 1000 g. of benzene gave, respectively, the computed values of 329, 328 and 336 for the molecular weight of dimethylgallium hydroxide. These values are reasonably close to the value 350.4 calculated for the molecule

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[1] Presented at the Symposium on Inorganic Polymers, Division of Physical and Inorganic Chemistry, at the Chicago Meeting of the American Chemical Society, September, 1953.

[2] Taken in part from the thesis submitted to the Graduate School, Cornell University, February, 1954, by M. E. Kenney in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

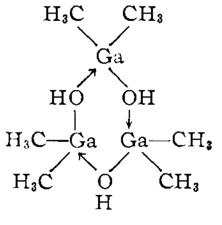
[3] General Electric Company Predoctoral Fellow, 1952–1953.

[4] (a) L. M. Dennis and W. Patnode, THIS JOURNAL, **54**, 182 (1932); (b) P. Brandt, Ph.D. thesis, Cornell University (1931); (c) G. Renwanz, *Ber.*, **65**, 1308 (1932); (d) C. Kraus and F. Toonder, *Proc. Natl. Acad. Sci., U. S.*, **19**, 292 (1933).

[5] Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929, p. 388.

[6] Mitchell and Smith, "Aquametry," Interscience Publishers, Inc., New York, N. Y., 1948.

$((CH_3)_2GaOH)_3$. This indicates that the compound exists as a trimer in benzene solution. It is, of course, possible that there is a mixture of different polymeric molecules in benzene, but this does not seem likely because the molecular weight values do not vary significantly with dilution, and because the compound crystallizes readily from solution rather than forming an oil or a glass. The six-membered ring structure



set up by donor–acceptor bonding and probably stabilized by resonance hybridization seems reasonable for this trimer. The properties of the crystalline compound are consistent with our belief that such cyclic discrete trimeric molecules are the structural units in the solid state as well as in solution.

Melting Point, Solubility and Density.—At 87 to 88.5° dimethylgallium hydroxide melts in the air to a colorless liquid which slowly gives off bubbles of gas. As the evolution of gas progresses the liquid phase rapidly becomes very viscous.

The hydroxide is not appreciably soluble in water but is quite soluble in carbon tetrachloride, cyclohexane, benzene, chloroform and petroleum ether, as would be expected for the cyclic molecular structure postulated above.

The density of the compound, determined by the displacement of Nujol saturated with the hydroxide is 1.75 g./cm.^{3} at 25°.

Crystallographic Data.—Crystals suitable for microscopic examination were obtained directly on slides by recrystallization of the hydroxide from benzyl acetate. The crystals are biaxial, optically positive, and show regular polarization colors. They are probably monoclinic. The indices are $\alpha = 1.529$, $\beta = 1.550$ and $\gamma = 1.592$ when measured with white light, and are related to the crystal faces as shown in Fig. 2.

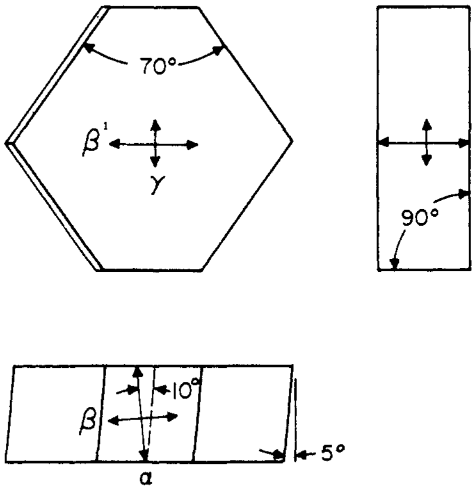


Fig. 2.—Orthographic projection of a typical crystal of $(CH_3)_2GaOH$.

The powder X-ray diffraction pattern of the hydroxide was obtained with Cu Kα radiation using a nickel filter. The *d* spacings calculated for the stronger lines are listed in Table I, along with the visually estimated intensities.

Dipole Moment.—The heterodyne beat method was used for this work and the data are given in Table II.

The values of the molar polarization and molar refraction of the hydroxide were computed from the experimental data by the method described by Smyth.[7] Taking 131 as the value for the molar polarization (since no significant trend in the values is apparent) and 66 as the molar refraction, the dipole moment turns out to be 1.8 debyes if no allowance is made for the atomic polarization.

TABLE I

POWDER X-RAY DIFFRACTION FOR $((CH_3)_2GaOH)_3$

d	Estimated intensity	*d*	Estimated intensity
6.88	Medium	3.21	Weak
6.09	Medium	2.94	Weak
5.02	Strong	2.62	Weak
4.28	Medium	2.46	Weak
3.76	Strong	2.36	Weak

TABLE II

DIPOLE MOMENT OF $((CH_3)_2GaOH)_3$ IN BENZENE AT 25°

f_2	ϵ	*d*	P_2	$P_{\text{orientation}}$	μ
		Benzene			
	2.275	0.8731			
		$((CH_3)_2GaOH)_3$			
0.01158	2.321	0.8912	130		
.00671	2.302	.8836	131		
.004866	2.294	.8806	132	65	1.8

Models of the six possible isomers of the six-membered ring molecule, constructed using tetrahedral bonding for the gallium atoms and pyramidal bonding for the oxygen atoms, are not symmetrical. Since a molecule with unsymmetrically positioned polar groups has a permanent dipole moment, the observed dipole of the hydroxide is consistent with the postulated ring structure.

Reactivity of Dimethylgallium Hydroxide.—When the compound is heated in a nitrogen atmosphere at 150° methane is released in the ratio of one molecule of methane for each atom of gallium. The reaction apparently begins at the melting point of the compound but requires about six hours heating at 150° for completion. The non-volatile residue left behind is a glassy isotropic material, insoluble in benzene, carbon tetrachloride, ether and water. The stoichiometry of the thermal decomposition is such that it seems very likely that this residue is a highly polymeric methylgallium oxide and that the over-all reaction may be summarized by the equation

$$n((CH_3)_2GaOH)_3 = 3nCH_4 + (MeGaO)_{3n}$$

When dimethylgallium hydroxide is suspended in water there is very little reaction at room temperature but at 60° a gas that has been identified as methane by its infrared spectrum is slowly evolved. When held for 60 hours at 60° there was released about 90% of the methane required if the thermal decomposition reaction given above were taking place.

When the crystalline hydroxide is exposed to dry oxygen at room temperature for a day and then at 60° for an hour, no appreciable quantity of oxygen is absorbed and no change in the infrared spectrum of the solid is observed.

Discussion

All of the observed properties of dimethylgallium hydroxide are consistent with the trimeric cyclic structure suggested. The resistance of the compound to oxidation and hydrolysis is to be expected from the polymeric structure. Oxidation or hydrolysis probably would have to take place by initial coördination of the reactant with the gallium atoms. But in the ring structure each gallium already has a coördination number of four and this presumably will protect the substance against oxidation and hydrolysis.

It is not known for sure what the solid end products of the thermal decomposition and hydrolysis are, but it seems very likely that they may be polymeric $(CH_3GaO)_n$. This might be the discrete trimeric molecule

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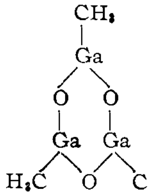
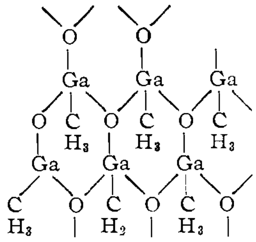
(7) C. P. Smyth, "Determination of Dipole Moments," in "Physical Methods of Organic Chemistry," ed. by A. Weissberger, Interscience Publishers, Inc., New York, N. Y., Part II, 1621.



formed by the reaction of methyl groups with adjacent hydrogens in the hydroxyl groups. This however appears to be ruled out by the non-volatile, inert and glassy nature of the residue. Instead, the decomposition may well involve intermolecular condensation, with the splitting out of methane and the production of highly cross-linked chains in the glass or of an endless gallium–oxygen puckered sheet framework with one methyl group attached to each gallium.

Construction of a model of such a high polymeric sheet molecule indicates that the methyl groups would be attached alternately on either side of the sheet to produce two hydrocarbon surfaces sandwiching the puckered gallium–oxygen framework.



As a result of this investigation it is seen that dimethylgallium hydroxide behaves quite differently from the organo monohydroxy compounds of boron and silicon which condense very readily with the splitting out of water. Cyclic boron–oxygen and silicon–oxygen frameworks are obtained by the intermolecular splitting out of water from diol molecules.

ITHACA, N. Y.

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

Dielectric Constants of Liquid Chlorine Trifluoride and Iodine Pentafluoride[1]

BY MAX T. ROGERS, H. BRADFORD THOMPSON AND JOHN L. SPEIRS

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The dielectric constants of chlorine trifluoride and iodine pentafluoride have been measured in the range 0 to 42° at several frequencies and may be expressed by the equations $\epsilon_t = 4.754 - 0.018t$, for chlorine trifluoride, and $\epsilon_t = 41.09 - 0.198t$, for iodine pentafluoride. The results indicate that these substances are associated in the liquid state.

Introduction

Considerable interest has arisen concerning the solvent properties of halogen fluorides, and it has been proposed that some of them may be associated liquids.[2,3] In the present study the dielectric constants of chlorine trifluoride and iodine pentafluoride have been determined and the results have been considered with respect to liquid structure.

Experimental

Electrical Apparatus.—Determination of dielectric constants was carried out using a General Radio Twin-T impedance bridge with a stable signal generator and a communications receiver. Due to the high specific conductance (approximately 2×10^{-5} ohm^{-1} cm.$^{-1}$) of iodine pentafluoride, it was necessary to extend the conductance range of the instrument to achieve a balance. This was accomplished by addition of a 400 $\mu\mu$f. variable capacitor in parallel with the conductance balance capacitor. As the dielectric constant is obtained from the susceptance, rather than the conductance, of the sample, the readings of this capacitor were not used in the calculations described below. Frequencies were measured using a calibrated BC 221-O frequency meter.

Cells.—Two different cells were used, both of which were arranged to plug directly into the sockets of the Twin-T bridge, thus minimizing the distributed capacitance and inductance of the leads. Internally the cells were of nickel construction and the electrical insulation of the central electrode, as well as the vacuum sealing of the lead, were accomplished by a Teflon bearing and packing gland.

The larger cell, used for chlorine trifluoride, was arranged to permit use of a variety of central electrodes to obtain various replaceable capacitances reproducibly. The outer electrode was a hollow cylinder with removable end plates ground to seal against the vertical portion of the cylinder. The upper end of the central nickel electrode was centered in the Teflon bearing and the lower end was provided with a shaft which was carried through the Teflon stuffing box. The whole assembly was held together by a three piece outer aluminum jacket which was provided with ducts for circulation of water from a constant temperature bath. The smaller cell, used for iodine pentafluoride, was of particularly simple construction (Fig. 1). Both cells differ from conventional cell construction practice in that the outer grounded cylinder is also the container for the liquid; this reduces the volume of liquid required for a measurement and simplifies temperature regulation.

The cells were calibrated using benzene, chlorobenzene, nitrobenzene and water as standards. The larger cell had a replaceable capacitance of 143.5 $\mu\mu$f. and a series inductance of 0.045 μhenries, while these constants for the smaller cell were 10.32 $\mu\mu$f. and 0.02 μhenries, respectively.

Materials.—Chlorine trifluoride was purified by taking the center cuts of two successive simple distillations at room temperature. The cell was then evacuated and filled with the liquid, and a pressure of approximately two atmospheres (inert gas) was applied to cause the liquid chlorine trifluoride to fill all voids. Measurements were carried out on three different samples, with results agreeing within the limits reported. The low specific conductance of the chlorine trifluoride used, $<6 \times 10^{-9}$ ohm^{-1} cm.$^{-1}$, indicated the absence of conducting impurities, such as hydrogen fluoride, which might cause sizable errors due to its high molecular dipole moment.

The purification of iodine pentafluoride is described elsewhere.[1] Analysis of the freezing curve of the material used indicated that the total molal concentration of impurities was approximately 0.0025.

Treatment of Experimental Data.—An equivalent circuit for the experimental cell is represented by the combination

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[1] Physical Properties of the Halogen Fluorides. II. For preceding paper see M. T. Rogers, J. L. Speirs, H. B. Thompson, and M. B. Panish, THIS JOURNAL, **76**, 4843 (1954).

[2] K. Schafer and E. Wicke, *Z. Elektrochem.*, **52**, 205 (1948).

[3] E. A. Jones, T. F. Parkinson and R. B. Murray, *J. Chem. Phys.*, **17**, 501 (1949).