

curvature in the $\log \chi$ - $\log \alpha$ plot. Thus it is not certain what deviation, if any, would occur at $\alpha \geq 60$ and, if so, to what extent it deviates. The same argument can equally be applied to the $[\eta]$ - α plot. Therefore it is gratifying to find the good agreement between the experimental points (Fig. 3) and the extended theoretical values (broken lines), thus enabling one to use these extrapolated values with some confidence. The lower experimental values than the calculated ones in curve 3 were at least partly due to the significant experimental errors at high shearing stresses. Similar strikingly good agreement was also found between extrapolated theoretical values and experimental points for PBLG No. 416 in the previous publication² even for a 20-fold extension of α (to 1200) (figure not shown here). Nevertheless, the possible uncertainty involved in the extrapolation as mentioned above could be very serious and should be used with reservation unless future experiments indicate otherwise.

NOTE ADDED IN PROOF.—Professor J. J. Hermans has kindly pointed out that the viscosity at the capillary wall, η , can be obtained by straightforward

differentiation and represented as

$$1/\eta = (1/\pi R^3 r^3) d(Qr^3)/dr$$

the symbols having the same meaning as those in eq. 1 and 2 (see also, J. Hermans, Jr., and J. J. Hermans, *Proc. Koninkl. Ned. Akad. Wetenschap.*, **B61**, 324 (1958)). It can be shown that the above equation also yields eq. 3 but without assuming a power law (eq. 6). Thus eq. 3 becomes perfectly exact. In a recent note Reichmann (*J. Phys. Chem.*, **63**, 638 (1959)) has also discussed the effect of polydispersity on non-Newtonian viscosity. Philippoff and Gaskins (*ibid.*, **63**, 985 (1959)) have reinterpreted the author's earlier data (ref. 2) in the light of the power law of viscosity.

Acknowledgments.—The author is indebted to Dr. E. R. Blout and Professor P. Doty for their generous supply of the polypeptide samples. He wishes to thank Dr. E. Passaglia for stimulating discussions. Thanks are also due Mr. F. P. Conover for carrying out the viscosity measurements.

MARCUS HOOK, PENNSYLVANIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

The Structure of the Cyclic Tetramer of Dimethylgallium Hydroxide¹

BY GORDON S. SMITH AND J. L. HOARD

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The monoclinic unit of structure of dimethylgallium hydroxide has $a = 8.62 \pm 0.01$, $b = 12.14 \pm 0.04$, $c = 8.50 \pm 0.02$ Å., $\beta = 92.05 \pm 0.10^\circ$, $P2_1/c$ as space group, and contains $8\text{Me}_2\text{GaOH}$. Patterson, Fourier and difference syntheses of photographically recorded X-ray intensity data from the three principal zones of reflection lead to determination of structure. The characteristic species in the crystal is the cyclic tetramer (Fig. 3) of $\bar{1}$ symmetry with hydroxyl oxygen and gallium atoms forming an eight-membered central ring. Averaged values of bond lengths are $\text{GaO} = 1.96$, $\text{GaC} = 1.97$ Å. and of bond angles are $\text{OGaO} = 98.8$, $\text{GaOGa} = 133.1$, $\text{CGaC} = 129.2$, $\text{CGaO} = 106.2^\circ$. The compact molecules pack together closely in the crystal.

Introduction

Kenney and Laubengayer² prepared dimethylgallium hydroxide as monoclinic crystals soluble in a variety of organic solvents and melting with accompanying slow decomposition at 87 to 88.5° . Cryoscopic and dipole moment measurements on benzene solutions led to the trimeric formula $(\text{Me}_2\text{GaOH})_3$ and a moment of 1.8 debyes for the solute molecule. Both in solution (cyclohexane, carbon tetrachloride) and in a Nujol mull, the compound showed strong infrared absorption bands attributable to OH. These data led the authors² to postulate the cyclic trimer with gallium and hydroxyl oxygen atoms alternating around a central six-membered ring as the characteristic species in solution and probably also in the crystal. The related but thermally more stable compounds $(\text{Me}_2\text{GaXMe})_n$, in which $\text{X} = \text{O}, \text{S}, \text{Se}$, were found³ to be dimeric in the vapor phase and were assigned³ a structure with Ga and X atoms alternating about a central four-membered ring.

The X-ray diffraction study now reported shows that the characteristic molecular species in crystalline dimethylgallium hydroxide is in fact the cyclic tetramer of Fig. 3.

Experimental

Slow evaporation of cyclohexane solutions of purified dimethylgallium hydroxide, kindly furnished by Dr. Kenney,² gave well-developed crystals having the aspect of rhomboidal plates. When exposed to the atmosphere the initially colorless crystals slowly developed a white coating insoluble in cyclohexane. The useful life of all specimens used for X-ray study was prolonged by means of a protective coating of polyisobutylene.

All X-ray data were photographically recorded using $\text{Cu K}\alpha$ radiation filtered through nickel foil. The unit cell data are as follows: diffraction symmetry, $2/m$; lattice constants, $a = 8.62 \pm 0.01$, $b = 12.14 \pm 0.04$, $c = 8.50 \pm 0.02$ Å., $\beta = 92.05 \pm 0.10^\circ$; density, measured² as 1.75 g./cc., calculated as 1.74 g./cc. assuming eight monomeric molecules within the cell; space group, $P2_1/c$. The presence of a few weak reflections forbidden by the glide plane was in all cases convincingly explained⁴ in terms of double reflection,⁵ and the subsequent structure analysis was in all details compatible with the space group $P2_1/c$.

(1) Supported in part by National Science Foundation Research Grant NSF-G5924.

(2) M. E. Kenney and A. W. Laubengayer, *THIS JOURNAL*, **76**, 4839 (1954).

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

(4) For details of this analysis see Gordon S. Smith, "The Crystal Structure of the Cyclic Tetramer of Dimethylgallium Hydroxide," Cornell University Thesis, Cornell University Library, 1957.

(5) M. Z. Renninger, *Z. Krist.*, **97**, 95 (1937); *Z. Physik*, **106**, 147 (1937).

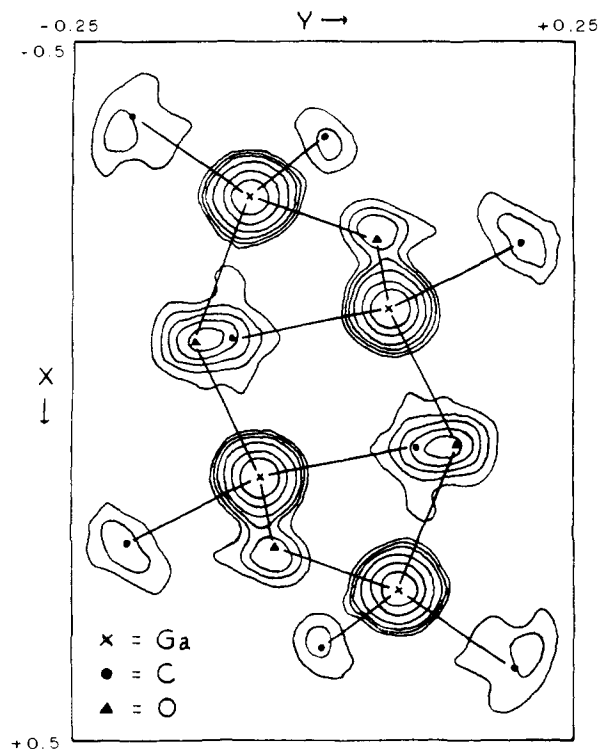


Fig. 1.—Projected electron density, $\rho(x,y)$, for half the unit cell. The framework of the tetrameric molecule centered at the origin is indicated.

Specimens used for the collection of intensity data were carefully cut from larger crystals parallel to the desired axes and were gently ground to approximately cylindrical form. Specimens cut along the a , b , c axes had diameters, respectively, of 0.39, 0.34, 0.34 mm. Reflection intensities were collected using the triple film technique at two exposure times and were estimated visually by comparison with a standard intensity scale prepared with one of the specimen crystals. These intensities were corrected for variation of absorption⁶ with scattering angle and converted to relative $|F|^2$ values in the usual manner.⁷ A total of 121 $hk0$, 81 $h0l$, and 108 $0kl$ forms were recorded with Cu $K\alpha$ radiation.

Determination of Structure.—The space group $P2_1/c$ offers⁸ fourfold general positions requiring no symmetry and two fold special positions requiring a center of inversion. It was not surprising to find that the Patterson syntheses required placement of the eight gallium atoms in two sets of fourfold positions since (1) the monomeric species Me_2GaOH could not have an inversion center and (2) no reasonable polymerization scheme which would allow gallium atoms to lie in inversion centers could be devised. Analysis of the principal features of the three Patterson projections led to a self-consistent assignment of gallium positions. Neither at this nor at any later stage of the analysis did any subtleties of interpretation appear to require description in terms of $P2_1$ rather than $P2_1/c$. (The presence of either a true twofold axis or a true mirror plane was wholly incompatible with the Patterson syntheses.)

(6) "Internationale Tabellen zur Bestimmung von Kristallstrukturen." Zweiter Band. Gebrueder Borntraeger, Berlin, 1935.

(7) Cf. H. Lipson and W. Cochran, "The Determination of Crystal Structures. The Crystalline State," Vol. III, G. Bell and Sons Ltd., London, 1953.

(8) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952.

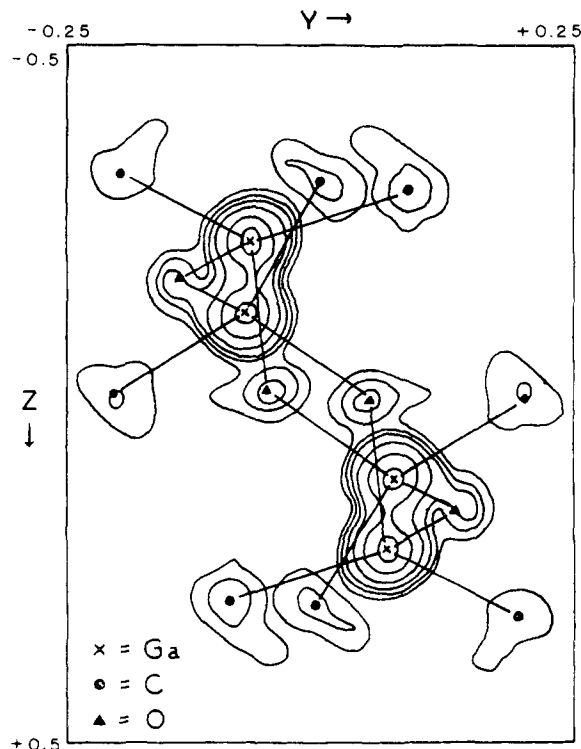


Fig. 2.—Projected electron density, $\rho(y,z)$, for half the unit cell. The framework is indicated for the same molecule as in Fig. 1.

The calculated contributions of gallium atoms proved to be phase determining for a sufficient fraction of the reflection amplitudes as to permit construction of the three Fourier projections of electron density by the usual methods⁷ of successive approximation. Figures 1 and 2 reproduce the respective projections $\rho(x,y)$ and $\rho(y,z)$ with indication of their interpretation in terms of the cyclic tetrameric molecular model of Fig. 3. The atomic positions marked on Figs. 1 and 2 are those resulting from further refinement of the structural data through Fourier difference syntheses.⁷

Contours of a gallium peak in Fig. 1 are nearly concentric and circular, while those of the resolved carbon atoms suggest rather large and anisotropic thermal motions. However, the larger part of the irregularity of contour and the apparent anisotropy of thermal motion for the light atoms proved to be the result of strong diffraction rippling emanating from the nearby gallium peaks. The $\rho-\rho_c$ syntheses, using for each zone a single isotropic thermal parameter (B) in computing⁹ the amplitudes (F_c) synthesized in ρ_c gave quite satisfactory results at and near the positions of most of the minor peaks. The isotropic thermal parameter and scale factor (to put experimental amplitudes (F) on an absolute basis) were obtained for each set of zonal data from the least squares fitting of a plot of $\log \langle F_c/F \rangle$ vs. $\langle \sin^2\theta/\lambda^2 \rangle$, the indicated averages being taken over successive bands of width 0.05 \AA^{-1} in $\sin \theta/\lambda$. The $hk0$ and $0kl$ data were subjected to several cycles of refinement through

(9) The atomic form factors used were those of J. Berghius, I. M. Haanapel, M. Potters, B. O. Loopstra, C. H. MacGillavry and A. I. Veenendaal, *Acta Cryst.*, **8**, 478 (1955).

difference synthesis with accompanying marked improvement in the quality of agreement between observed and calculated reflection amplitudes. Final values of the thermal parameter for the $hk0$, $0kl$ and $h0l$ data were 2.04, 2.50 and 2.7 Å.², respectively. The indicated variations in B may be mostly the result of uncertainties in making absorption corrections on the only approximately cylindrical specimens.

The final atomic coordinates of the structure (Table I) were used to calculate amplitudes for all reflections accessible to measurement with Cu K α radiation. The calculated values were substantially larger than those observed for a few reflections of particularly large structure factor but very simple indices, *i.e.*, just those reflections expected to be most subject to extinction. The data were otherwise free of any suggestion of significant discrepancy between calculated and observed amplitudes.¹⁰ With all reflections accessible to Cu K α radiation included and with $||F|-|F_c||$ taken as $|F_c|$ for unobserved reflections (*i.e.*, the least favorable calculation), the values of $R = \Sigma||F|-|F_c||/\Sigma|F|$ computed for the $hk0$, $h0l$, $0kl$ zones, respectively, were 0.138, 0.162, 0.178. With the single modification of putting $|F|$ equal to $|F_c|$ for eight reflections showing pronounced extinction the respective R -values became 0.105, 0.122, 0.123.

TABLE I

PARAMETER DATA FOR THE (Me ₂ GaOH) ₄ STRUCTURE							
Atom	x	y	z	Atom	x	y	z
Ga ₁	-0.120	0.065	0.221	C ₁	-0.213	0.196	0.318
Ga ₂	.282	.073	.122	C ₂	.394	.188	.006
O ₁	.074	.133	.167	C ₃	.366	-.004	.303
O ₂	-.217	.052	.006	C ₄	-.078	-.088	.295

Discussion of the Structure

The tetrameric molecule of Fig. 3 has a center of inversion, $\bar{1}$, with some approximation to the higher symmetry of $2/m$. Using the notation $A_n, A_{\bar{n}}$ to denote a pair of atoms related through $\bar{1}$, the derived bond lengths are (Å.)

O₂Ga₁, 1.99; Ga₁O₁, 1.94; O₁Ga₂, 1.98; Ga₂O₂, 1.94; Ga₁C₁, 1.97; Ga₁C₄, 1.99; Ga₂C₂, 1.98; Ga₂C₃, 1.92. Standard deviations,⁷ σ : GaO, 0.028 Å., GaC, 0.036 Å.

The bond angles are (degrees)

O₂GaO₁, 98.9; O₂Ga₂O₂, 98.6; Ga₂O₂Ga₁, 133.0; Ga₁O₁Ga₂, 133.2; C₁Ga₁C₄, 133.8; C₂Ga₂C₃, 124.5; O₂Ga₂C₁, 106.5; O₁Ga₁C₁, 97.1; O₂Ga₁C₄, 106.4; O₁Ga₁C₄, 108.8; O₁Ga₂C₂, 107.3; O₂Ga₂C₃, 99.3; O₁Ga₂C₃, 110.0; O₂Ga₂C₂, 114.2. Range of σ : 1.2–2.0°.

Taken at face value, the observed alternation between 1.94 and 1.98 or 1.99 Å., of successive GaO bond lengths around the ring corresponds to recognizable monomeric molecules held in tight association to give the tetramer. However, the maximum difference in bond length, 0.05 Å., as compared with a standard deviation of 0.028 Å.,

(10) Following submission with the ms. for inspection by referees, Amplitude Data for (Me₂GaOH)₄ have been deposited as Document number 5865 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting \$1.25 for photoprints, or \$1.25 for 35 mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

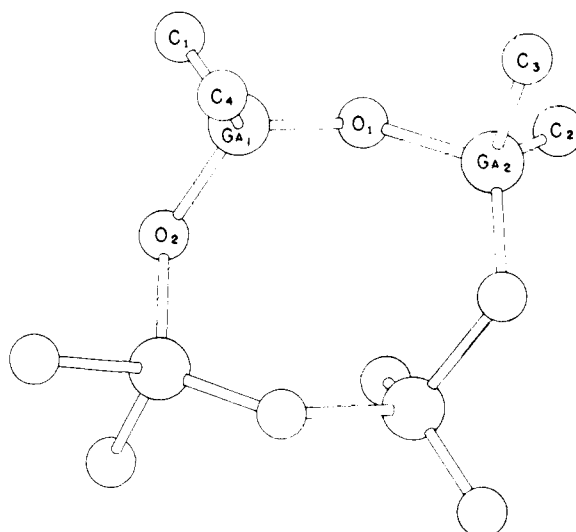


Fig. 3.—Model of the tetrameric molecule, (Me₂GaOH)₄, of $\bar{1}$ symmetry. Atoms C₁, C₄, Ga₁, Ga₂, C₂, C₃ lie in or very near to a *quasi*-mirror plane.

is just on the edge of possible significance.⁷ Stated somewhat differently, the maximum deviation of any GaO bond length from the mean is less than the standard deviation and has no statistical significance. No significant variations in carbon-gallium bond lengths are expected *a priori*, and although one bond distance (Ga₂C₃ = 1.92 Å.) departs from the mean (1.965 Å.) by more than the standard deviation (0.036 Å.), the difference falls short of attaining objective possible significance.

As compared with averaged bond lengths of GaO = 1.96, GaC = 1.97 Å., the sums of the covalent radii¹¹ are, respectively, 1.92, 2.03 Å. The comparison suggests that the GaMe bonds are a bit stronger than normal and that ring bonds involving hydroxyl rather than oxide oxygen may be relatively weak. Indirect evidence for the reality of this latter effect is provided by the structural data for octamethylcyclotetrasiloxane,¹² (Me₂-SiO)₄, with a molecular configuration of symmetry $\bar{1}$ generally similar to that of (Me₂GaOH)₄. For (Me₂SiO)₄, bond distances of SiO = 1.65, SiC = 1.92 Å., and bond angles of OSiO = 109°, SiOSi = 142.5°, CSiC = 106° are reported.¹² The observed difference of 0.37 Å. between SiO and SiC bond lengths is in marked contrast with the virtual equality of GaO and GaC distances in (Me₂GaOH)₄, and the obvious, if not unexpected, conclusion is that hydroxyl forms weak ring bonds as compared with oxide oxygen.

Objectively significant differences in the bond angles for the pair O₂Ga₂C₁ (106.5°) and O₁Ga₁C₁ (97.1°), and also for the pair O₁Ga₂C₂ (107.3°) and O₂Ga₂C₃ (99.3°), eliminate the possibility that the molecule in the crystal conforms within experimental error to the higher symmetry of $2/m$. Even so, it is useful to have the averaged bond angles for the simplest configuration of highest *quasi*-symmetry. The four bond angles obtained

(11) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948.

(12) H. Steinink, B. Post and I. Fankuchen, *Acta Cryst.*, **8**, 420 (1955).

are OGaO , 98.8° ; GaOGa , 133.1° ; CGaC , 129.2° ; CGaO , 106.2° . The departure from a regular tetrahedral distribution of bonds emanating from gallium, concentrated in a closing (*ca.* 10°) of the OGaO angle and an opening (*ca.* 20°) of the CGaC angle from the standard (109.5°) value is in marked contrast with the more conventional behavior of silicon (*vide supra*) in $(\text{Me}_2\text{SiO})_4$. Viewed purely as a steric problem it would appear that the substantially longer bond distance in the ring of $(\text{Me}_2\text{GaOH})_4$ permits smaller ring bond angles leading both to a relatively more compact arrangement and to minimization of steric repulsive forces between hydroxyl hydrogen and methyl hydrogen atoms. The larger external bond angles of $(\text{Me}_2\text{GaOH})_4$ give a separation of about 3.5 Å. for the two methyl groups attached to the same ring atom, a non-trivial gain of about 0.4 Å. over $(\text{Me}_2\text{SiO})_4$ in terms of a van der Waals packing radius of about 2.0 Å. for methyl.¹¹ Similarly large CMC bond angles external to a central four-membered ring are reported for dimethylaluminum chloride dimer¹³ and for trimethyl-aluminum dimer.¹⁴

The most interesting feature of the intramolecular packing within the $(\text{Me}_2\text{GaOH})_4$ molecule centers on the equivalent methyl groups of C_4 and C_4 . The pertinent interatomic distances are (Å.): C_4Ga_1 (bonded), 1.99; C_4Ga_1 , 4.77; C_4Ga_2 , 3.99; C_4Ga_2 , 3.90; C_4C_2 , 3.87; C_4C_3 , 3.96; C_4O_1 , 3.97; C_4O_2 , 3.70. It is evident that the methyl groups of C_4 and C_4 pack into the "holes" on opposite faces of the ring; moreover, it appears probable that these groups key into the ring in a manner which requires abandonment of $2/m$ in favor of $\bar{1}$ for the molecular symmetry. An unstrained packing model complete except for one hydrogen each on C_4 and C_4 is readily put together in accordance with $2/m$. Addition of these hydrogens, either with a C_4H bond pointing toward or away from Ga_1 , produces interference with O_1 and O_2 (for the opposite face, read C_4H , Ga_1 , O_1 and O_2 , respectively) to give a model in mechanically unstable equilibrium. Application at Ga_2 and Ga_2 of a small oscillatory twisting about the twofold axis allows the model to settle irreversibly into a configuration which, in respect to the Ga, O and C positions, is essentially that derived experimentally. During this process the methyl groups of C_4 and C_4 rotate through approximately 30° while maintaining $\bar{1}$ symmetry so that a C_4H bond points directly at O_1 . The accompanying deformation of the ring, which is propagated through rotation about ring bonds, leaves C_4O_1 (3.97 Å.) a good deal longer than C_4O_2 (3.70 Å.) with O_2 approaching C_4 so as to remain virtually equidistant (*ca.* 3.4 Å.) from two hydrogen atoms.¹⁵

(13) K. J. Palmer and N. Elliott, *THIS JOURNAL*, **60**, 1852 (1938).

(14) P. H. Lewis and R. E. Rundle, *J. Chem. Phys.*, **21**, 986 (1953). In this case, the rather unfashionable principle that methyl-methyl contacts throughout the molecule should be equalized and maximized (the connexity of atoms and bond lengths being given) yields nearly the observed bond angles, including the AlCAL angle of 70° within the ring.

(15) It may be noted that deformation of the $2/m$ model to give the observed Ga-O-C framework would seem to follow also on the im-

This analysis indicates that $\bar{1}$ probably is the natural point group of the free tetrameric molecule. The experimentally determined departure of the ring from $2/m$ is formally attributable to shifts in oxygen positions. Gallium atoms outline a rhombus of acute angle, 80.1° , and edge, 3.60 Å. To conform to $2/m$ the oxygen atoms should define a rectangle (becoming a square for a single GaO bond length), and the planes determined by the respective oxygen and gallium atoms should intersect in the diagonal Ga_2Ga_2 of the rhombus, *i.e.*, in the unique axis of twofold symmetry. However, the oxygen atoms in fact outline a rhombus of acute angle, 83° , and edge, 2.98 Å. The dihedral angle between the planes of the two rhombi is about 31° .

As suggested by the behavior of the thermal parameter (*vide supra*), the arrangement of the compact molecules within the crystal is noteworthy for a rather uniformly tight packing irrespective of direction. A general idea of the molecular packing is obtained from Fig. 1, which shows one tetramer centered at the origin and taking up just half of the cell ($-a/2$ to $a/2$, $-b/4$ to $b/4$, $-c/2$ to $c/2$). The molecular shape and orientation allow a well-matched fitting of successive molecules along x to give formally an infinite chain. These chains stack in exact superposition along z with all tetramer centers in the plane $y = 0$. The glide plane $y = 1/4$ (or $-1/4$) generates an enantiomorphic stack in parallel array with tetramer centers in $y = 1/2$ (or $-1/2$) but displaced uniformly by $c/2$ along z as compared with the reference stack. Thus successively enantiomorphic stacks along y are interwoven along y and z to complete the packing in three dimensions. The numerous methyl-methyl contacts between molecules lie in the range 4.0-4.2 Å., methyl-oxygen contacts in the range 3.4-3.6 Å.

Although the reported² cryoscopic measurements leading to the assignment of the trimeric formula to dimethylgallium hydroxide in benzene solution covered too narrow a concentration range to be altogether convincing, re-examination of the data does not encourage an alternative interpretation in terms of an equilibrium mixture of tetrameric with dimeric and/or monomeric species. The dipole moment data strongly favor a species in solution, such as the postulated³ cyclic trimer, which lacks a center of inversion. A cyclic trimer with a flat ring and bond angles of about 133° for GaOGa and 107° for OGaO would show less methyl-methyl interaction and would be generally more open in structure than the tetramer. It seems reasonable that this more open structure would be favored in solution, at least whenever interaction with the solvent molecules is fairly strong. Probably, however, the high packing density of the crystalline tetramer is well beyond the reach of any ordered arrangement of trimers. The published² data suggest that the activation energies associated with making and breaking ring bonds cannot be very large.

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probable assumption that the C_4H bond points toward O_2 , *i.e.*, that the 3.70 Å. C_4O_2 separation is interpreted as a hydrogen bond.