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SYNTHESIS AND CHARACTERIZATION OF MESITYLGALLIUM
CHLORIDE COMPOUNDS INCLU (U) STATE UNIV OF NEW YORK AT
BUFFALO DEPT OF CHEMISTRY O T BEACHLEY ET AL

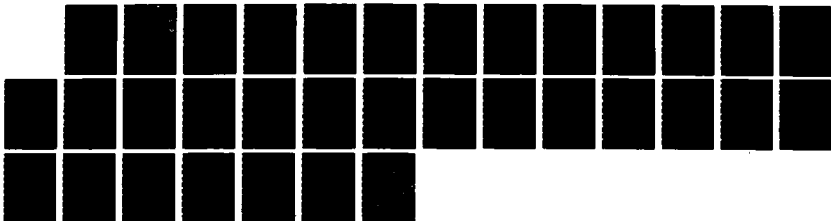
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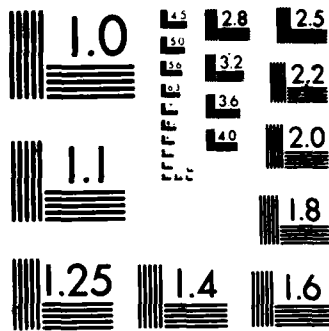
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unusually high melting solid which is insoluble in hydrocarbon solvents and crystallizes in the centrosymmetric monoclinic space group, $P2_1/m$ (C_{2h}^2 ; No 11) with $a = 8.3989(21)$, $b = 6.9976(19)$, $c = 18.0347(57)$ Å, $\beta = 100.159(23)^\circ$, $V = 1043.3(5)$ Å³ and $Z = 4$ (formula units). Diffraction data (Mo K α , $2\theta = 5.0-45.0^\circ$) were collected with a Syntex $P2_1$ diffractometer and the structure was refined to $R_F = 6.2\%$ for all 1502 independent reflections.

Dichloromesitylgallium(III) is a one-dimensional polymer in which planar Ga(mesityl)Cl units are linked by bridging chloride ligands. The correct formulation is $[Ga(C_6H_2Me_3)Cl(\mu-Cl)]_n$. Distances of interest include Ga...Ga = 3.781(1)Å, Ga-Cl(terminal) = 2.150(4)-2.164(4)Å, Ga-Cl(bridging) = 2.363(3)-2.369(3)Å and Ga-C(mesityl) = 1.943(12)-1.970(14)Å.

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Abstract

The mesitylgallium chloride compounds, GaMes_2Cl and GaMesCl_2 , have been prepared and fully characterized by melting point data, elemental analyses, solubility properties, IR and ^1H and ^{13}C NMR spectroscopic data and Lewis acidity studies. Cryoscopic molecular weight studies of GaMes_2Cl in benzene solution are consistent with the presence of dimeric molecules. Lewis bases such as Et_2O and THF react with $(\text{GaMes}_2\text{Cl})_2$ in benzene to establish two equilibria which are consistent with the presence of the dimer, a monochloride bridged 2:1 adduct $[(\text{GaMes}_2\text{Cl})_2 \cdot \text{base}]$ and the 1:1 adduct. The dichloro derivative GaMesCl_2 is an unusually high melting solid which is insoluble in hydrocarbon solvents and crystallizes in the centrosymmetric monoclinic space group $P2_1/m$ (C_{2h}^2 ; No 11) with $a = 8.3989(21)$, $b =$

6.9976(19), $c = 18.0347(57)\text{\AA}$, $\beta = 100.159(23)^\circ$, $V = 1043.3(5)\text{\AA}^3$ and $Z = 4$ (formula units). Diffraction data (Mo K α , $2\theta = 5.0-45.0^\circ$) were collected with a Syntex P2₁ diffractometer and the structure was refined to $R_F = 6.2\%$ for all 1502 independent reflections. Dichloromesitylgallium(III) is a one-dimensional polymer in which planar Ga(mesityl)Cl units are linked by bridging chloride ligands. The correct formulation is $[\text{Ga}(\text{C}_6\text{H}_2\text{Me}_3)\text{Cl}(\mu\text{-Cl})]_n$. Distances of interest include $\text{Ga}\cdots\text{Ga} = 3.781(1)\text{\AA}$, $\text{Ga-Cl}(\text{terminal}) = 2.150(4)\text{-}2.164(4)\text{\AA}$, $\text{Ga-Cl}(\text{bridging}) = 2.363(3)\text{-}2.369(3)\text{\AA}$ and $\text{Ga-C}(\text{mesityl}) = 1.943(12)\text{-}1.970(14)\text{\AA}$.

Introduction

The presence of bulky organic substituents on main-group elements leads to a variety of interesting and unusual chemical properties. Four mesityl (Mes) groups served to stabilize the first fully characterized compound with a silicon-silicon double bond, $^1\text{Si}_2\text{Mes}_4$. In group 13 chemistry, the effects of bulky substituents are just beginning to be elucidated. In indium(I) chemistry, the bulky pentamethylcyclopentadienyl group produced a hydrocarbon soluble, golden yellow solid which had a structure based upon an apparent octahedral cluster of $\text{In}_6(\text{C}_5\text{Me}_5)_6$ with indium(I) atoms on the interior and $\eta^5\text{-C}_5\text{Me}_5$ groups on the exterior.² In contrast, $\text{In}(\text{C}_5\text{H}_5)$ has been described as a hydrocarbon insoluble, yellow solid with a zig-zag polymeric structure.³ When the typical compounds of the heavier group 13 elements are considered, the primary effects of the bulky substituents appear to be related to a reduction in their Lewis acidity. Triorganoaluminum compounds such as AlMe_3^4 and AlPh_3^5 are dimers but $\text{Al}(\text{t-Bu})_3^6$ and AlMes_3^7 are monomers. The X-ray structural study of AlMes_3 reveals significant interactions between ortho methyl groups.⁷

Trimesitylgallium⁸ is also monomeric in the solid state but this is not surprising because even GaMe₃ is a monomer.⁹ However, the Lewis acidity⁸ of GaMes₃ has been reduced so significantly that it does not form adducts with Et₂O or the stronger base, THF. Similar observations¹⁰ have been made for Ga(C₅Me₅)₃. Two pentamethylcyclopentadienyl groups on gallium also have significant effects. The compound Ga(C₅Me₅)₂Cl is monomeric in benzene solution¹¹ and it does not form Et₂O or THF adducts. However, the two C₅Me₅ groups are insufficient to prevent the formation of the typical dimer with chlorine bridges in the solid state. When the number of pentamethylcyclopentadienyl groups is reduced to one,¹¹ all properties of Ga(C₅Me₅)Cl₂ are consistent with an organogallium compound with small substituents.

In this paper, the synthesis and characterization of GaMes₂Cl and GaMesCl₂ are described. The characterization data for both compounds include melting points, elemental analyses, solubility properties, IR and ¹H and ¹³C NMR spectroscopic data and Lewis acidity studies. In addition, the X-ray structural study of GaMesCl₂ is described. The presence of bulky mesityl groups leads to unexpected observations. The compound GaMesCl₂ exists in the crystalline state as a linear chloride-bridged polymer, a novel structure in group 13 chemistry. The dimesityl derivative GaMes₂Cl reacts with the Lewis base diethyl ether to establish equilibria involving a minimum of three dimesitylgallium species.

Experimental Section

General Data: All compounds described in this investigation were extremely sensitive to oxygen and moisture and were manipulated in a standard vacuum line or in a purified argon atmosphere. Gallium(III)

chloride was purified by sublimation under high vacuum at 70-80°C immediately prior to use. Trimesitylgallium(III) GaMe_3 was prepared as previously described.⁸ All solvents were purified prior to use. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Infrared spectra of Nujol mulls between CsI plates were recorded by means of a Perkin-Elmer 683 spectrometer. Absorption intensities are reported with abbreviations w(weak), m(medium), s(strong), vs(very strong) and sh(shoulder). The ^1H NMR spectra were recorded at 90 MHz by using a Varian Model EM-390 spectrometer. Chemical shifts are reported in δ units (ppm) and are referenced to SiMe_4 at δ 0.00 and benzene at δ 7.13. The ^{13}C NMR spectra were recorded at 22.49 MHz by using a Joel FX-90Q spectrometer. Carbon-13 chemical shifts are referenced to dioxane at δ 66.5. All NMR tubes were sealed under vacuum. Molecular weights were measured cryoscopically in benzene solution by using an instrument similar to that described by Shriver.¹²

Synthesis of GaMe_2Cl : In a typical experiment, recrystallized GaMe_3 (2.469 g, 5.78 mmol) and GaCl_3 (0.508 g, 2.89 mmol) were placed in a 100 mL flask equipped with a Solv-Seal joint. Diethylether, 50 mL, was vacuum distilled onto the mixture of GaMe_3 and GaCl_3 and the reaction mixture was permitted to warm to room temperature. The resulting colorless solution was then stirred for 18h, after which time it was filtered through a fine glass frit. After the ether was removed by vacuum distillation, trace quantities of Et_2O and/or vacuum grease were removed by washing the product with one 40 mL portion of pentane. Additional GaMe_2Cl was obtained from the pentane soluble portion to yield dimesitylgallium(III) chloride GaMe_2Cl (2.396 g, 6.974 mmol, 80.5% yield) as a colorless powder. If additional purification of GaMe_2Cl is desired, the compound can be recrystallized from pentane.

GaMes₂Cl: mp 158-159.5°C. Anal. Calcd.: C, 62.93; H, 6.45; Cl, 10.32. Found: C, 62.99; H, 6.38; Cl, 10.39. ¹H-NMR (C₆D₆, δ): 6.62 (aromatic H, 2H), 2.40 (ortho Me, 6H), 2.07 (para-Me, 3H); d⁸-THF, δ: 6.68 (aromatic H, 2H), 2.39 (ortho, Me, 6H), 2.15 (para, Me, 3H). ¹³C-NMR (C₄H₈O₂, δ): 143.73 (β-aromatic C), 140.95 (α-aromatic C), 137.64 (δ-aromatic C), 127.79 (γ-aromatic C), 24.03 (ortho-Me), 20.03 (para-Me). IR (Nujol mull, cm⁻¹): 1755vw, 1731vw, 1720vw, 1598s, 1550m, 1404m, 1287m, 1237w, 1226w, 1025m, 950vw, 943w, 886vw, 875w, 853m, 841vs, 718w, 704w, 682vw, 587s, 562m, 540s, 496w, 489w, 344m, 335m, 320m, 280m, 263m, 244vs. Solubility: soluble in Et₂O, THF and benzene, slightly soluble in pentane. Cryoscopic molecular weight, formula weight GaMes₂Cl, 344 (obsd. mol. wt., obsd. molality, association): 696, 0.0364, 2.03; 679, 0.0285, 1.98; 679, 0.0209, 1.98.

Synthesis of GaMesCl₂: A benzene solution (5mL) of 1.308g GaMes₃ (3.061 mmol) was added by means of a side-arm dumper to a flask charged with 1.079g of GaCl₃ (6.130 mmol) dissolved in 45 mL of benzene. Initially, the reaction mixture was a colorless solution. However, within 15 min a small amount of white precipitate was observed. The reaction mixture was then stirred for 18h during which time a heavy white precipitate formed. The benzene was then removed by vacuum distillation and the white powder was washed with pentane to facilitate the removal of trace quantities of benzene. Within a few hours of the removal of the pentane and while the flask was still under high vacuum, the color of the product changed from white to slightly "off-white". Mesitylgallium(III) dichloride, GaMesCl₂, was isolated as an "off-white" powder (2.041g, 7.856 mmol, 84.5% yield). The compound, GaMesCl₂, may be further purified by vacuum sublimation at 140°C, however the sublimation product still maintains its "off-white"

appearance. Colorless crystals of GaMe_2Cl_2 suitable for X-ray analysis were grown by slow sublimation in a sealed tube at 126°C .

GaMe_2Cl_2 : mp. $199.0\text{-}201.5^\circ\text{C}$. Anal. Calcd.: C, 41.61; H, 4.27; Cl, 27.29. Found: C, 41.76; H, 4.47; Cl, 27.23. $^1\text{H-NMR}$ (d^8 -THF, δ): 6.74 (aromatic H, 2H), 2.48 (ortho-Me, 6H) and 2.20 (para-Me, 3H). $^{13}\text{C-NMR}$ ($\text{C}_4\text{H}_8\text{O}_2$): 144.56 (β -aromatic C), 138.86 (δ -aromatic C), 133.30 (α -aromatic C), 128.03 (γ -aromatic C), 23.93 (ortho-Me) and 20.08 (para-Me).

Solubility: Soluble in Et_2O and THF; insoluble in benzene and pentane. IR (Nujol mull, cm^{-1}): 1725vw, 1594m, 1552w, 1409w, 1290m, 1240w, 1156vw, 1037m, 880vw, 842vs, 830vw, 719w, 698w, 682vw, 671w, 589m, 560vw, 540m, 520w, 492vw, 396vs, 365sh, 330sh, 313w, 278w. Crystals of GaMe_2Cl_2 are extremely sensitive to air as evidenced by a rapid color change to brown.

Lewis Acidity Studies of GaMe_2Cl and GaMe_2Cl_2 : A weighed evacuated tube was charged with either a sample of GaMe_2Cl or GaMe_2Cl_2 . The tube was evacuated and reweighed to determine the mass of the gallium sample. A large excess of base (THF or Et_2O) was vacuum distilled into the tube. The resulting solution was stirred for 15 min. The excess base was then removed by vacuum distillation and the system was subjected to dynamic vacuum for an additional 15h. The tube was reweighed to determine if the change in mass indicated the formation of a stoichiometric adduct. A $^1\text{H-NMR}$ spectrum (benzene solution) of the material remaining in the reaction tube was used to confirm the results of the mass measurements. Both GaMe_2Cl and GaMe_2Cl_2 formed 1:1 adducts with THF which are stable at room temperature. Neither compound formed a stable 1:1 adduct with Et_2O . $\text{GaMe}_2\text{Cl}\cdot\text{THF}$: mass GaMe_2Cl 0.0705g, mass THF 0.0144g, mole ratio $\text{GaMe}_2\text{Cl}/\text{THF}$ 1.03. $^1\text{H NMR}$ (C_6H_6 , δ): 3.54 (THF), 2.54, 2.31, 2.16, 2.13, 2.09, 1.15 (THF). $\text{GaMe}_2\text{Cl}_2\cdot\text{THF}$: mass GaMe_2Cl_2 0.0764g, mass THF 0.0157g, mole ratio $\text{GaMe}_2\text{Cl}_2/\text{THF}$: 1.35. $^1\text{H-NMR}$

(C₆H₆, δ) 3.54 (THF, 4.1), 2.57 (o-Me, 5.6), 2.11 (p-Me, 3.0), 1.02 (THF, 4.1). See Results and Discussion section for an explanation of these data.

Collection of X-Ray Diffraction Data for Dichloromesitylgallium(III).

A transparent colorless crystal of approximate orthogonal dimensions 0.22 x 0.33 x 0.50 mm³ was selected for the structural analysis and was inserted into a thin-walled glass capillary under an inert atmosphere (Ar). The crystal was mounted and aligned on a Syntex P2₁ automated four-circle diffractometer. The determination of Laue symmetry, crystal class, unit cell parameters and the crystal's orientation matrix were carried out as described previously.¹³ Intensity data were collected with Mo K α radiation for $2\theta = 5.0-45.0^\circ$ using conditions described in Table I. Data were corrected for absorption and for Lorentz and polarization effects and were placed on an approximately absolute scale by means of a Wilson plot. The diffraction symmetry was 2/m (C_{2h}) with systematic absences of Ok0 for k = 2n+1 (only). Possible space groups are the non-centrosymmetric P2₁ (C₂²; No. 4) and the centrosymmetric P2₁/m (C_{2h}²; No. 11). Data were collected for the quadrants +h, +k, ±l and for +h, -k, ±l because of the possibility that b might be a polar axis (i.e., the space group could be P2₁). Intensity statistics later suggested that the structure was centric and this was confirmed by the successful solution of the structure in the higher-symmetry centrosymmetric space group P2₁/m. (It should be noted that all crystals of Ga(C₆H₂Me₃)Cl₂ that we examined, including the data crystal, gave rise to rather broad diffraction peaks characteristic of the crystals' possessing an unusually large mosaic spread; a very accurate structural determination was not anticipated.)

Solution and Refinement of the Structure of Dichloromesitylgallium(III).

All crystallographic calculations were carried out by using our locally-modified form of the Syntex XTL package of crystallographic programs. Calculated structure factors were derived from the analytical expression of the scattering factors for neutral atoms; $\Delta f'$ and $i\Delta f''$ terms were included for all atoms.¹⁴ The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$ where $1/w = \{[o(|F_o|)]^2 + [0.015|F_o|]^2\}$.

The structure was solved by direct methods (MULTAN)¹⁵ in space group $P2_1/m$ using parity-group renormalized $|E|$ -values. An "E-map" provided the positions of two independent gallium atoms in special positions 0.497, 1/4, 0.295 and 0.382, -1/4, 0.222. The remaining non-hydrogen atoms were located from difference-Fourier syntheses. Refinement of positional and isotropic thermal parameters for all non-hydrogen atoms converged with $R_F = 10.4\%$. The use of anisotropic thermal parameters and the inclusion of hydrogen atoms in calculated positions¹⁶ led to convergence with $R_F = 6.2\%$ for 142 variables refined against 1502 observed reflections. [$R_F = 5.7\%$ for those 1231 data with $|F_o| > 6o(|F_o|)$.] A final difference-Fourier map showed no unusual features ($\rho(\max) = 1.33e^-$ at 0.148, 1/4, -0.036). Positional parameters are listed in Table II.

Results and Discussion

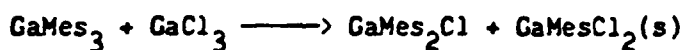
The mesitylgallium halides, $GaMes_2Cl$ and $GaMesCl_2$, have been prepared by stoichiometric ligand redistribution reactions between $GaMes_3$ and $GaCl_3$ and have been isolated in high yields. The two new compounds have been fully characterized by melting points, elemental analyses, solubility properties, cryoscopic molecular weight measurements, Lewis acidity studies as well as IR and 1H and ^{13}C NMR spectroscopic data. In addition, an X-ray

structural study of GaMe_2Cl has defined its crystal structure as a one-dimensional polymer.

The synthesis of GaMe_2Cl from a reaction mixture which had a stoichiometry of 2 mols of GaMe_3 per mol of GaCl_3 was facilitated by the use of Et_2O as the reaction solvent. Both reactants and the product were soluble but the product GaMe_2Cl did not form an adduct. It is also of interest that the final traces of ether were effectively removed by washing the product once with pentane. Pentane has also been attempted as a possible reaction solvent but its use is not recommended. The limited solubility of both GaMe_3 and GaMe_2Cl in pentane hinders the reaction from going to completion. Cryoscopic molecular weight measurements in benzene solution demonstrate that GaMe_2Cl exists as a dimer. Even though an X-ray structural study of this compound is not available, a chloride bridged dimer would be the most likely structure. This type of structure has been observed by X-ray structural studies of $[\text{Ga}(\text{C}_5\text{Me}_5)_2\text{Cl}]_2$,¹¹ $[\text{Ga}(\text{C}_5\text{Me}_5)\text{Cl}_2]_2$ ¹¹ and $(\text{GaCl}_3)_2$.¹⁷

Mesitylgallium dichloride has also been prepared in high yield by a stoichiometric ligand redistribution. Since the product has the stoichiometry of the combined reactants, great care must be taken when weighing and transferring the reactants to the reaction vessel. The preferred solvent for this reaction is benzene because both reagents are readily soluble and benzene has no Lewis base properties to gallium. Diethylether was also used as a reaction solvent but purification of the product was more difficult. The experimental observations after the reagents in a ratio of 1 mol of GaMe_3 to 2 mols of GaCl_3 were mixed in benzene were most unusual. Initially a clear solution was present. Then, after 15 min a small amount of white precipitate was observed. As the

reaction progressed, more and more precipitate formed. These observations suggest that the reactions as shown by the following equations are most likely slow. A slow ligand redistribution reaction of GaMes_3 would be



consistent with its low Lewis acidity due to the steric effects of the bulky mesityl groups.

The crystal of GaMesCl_2 consists of (theoretically infinite) strands of the one-dimensional polymer, $[\text{Ga}(\text{C}_6\text{H}_2\text{Me}_3)\text{Cl}(\mu\text{-Cl})]_n$. There are no short contacts between the strands. A section of one such strand is shown in Figure 1. The crystallographic "repeat unit" and atomic labelling are shown in Figure 2. This consists of a $\text{Ga}(\text{mesityl})\text{Cl}$ unit at $y = 1/4$ centered on $\text{Ga}(1)$, a $\text{Ga}(\text{mesityl})\text{Cl}$ unit at $y = -1/4$ centered on $\text{Ga}(2)$ and bridging chloride ligands ($\text{Cl}(12)$ at $y = 0$, and the symmetry related $\text{Cl}(12)(x, -1/2+y, z)$ at $y = -1/2$).

Interatomic distances and angles are collected in Table 3. The $\text{Ga}(1)\cdots\text{Ga}(2)$ separation is $3.781(1)\text{\AA}$ and the stacks of parallel mesityl ligands shown in Figure 1 have a repeat distance of $6.998(2)\text{\AA}$ (i.e., the b -dimension of the unit cell). Each gallium atom is tetrahedrally surrounded by four groups--a terminal chloride, two bridging chlorides and an η^1 -mesityl ligand. $\text{Ga}-\text{Cl}(\text{terminal})$ distances are $\text{Ga}(1)-\text{Cl}(1) = 2.150(4)$ and $\text{Ga}(2)-\text{Cl}(2) = 2.164(4)\text{\AA}$ (average = $2.157 \pm 0.010\text{\AA}$); the $\text{Ga}-\text{Cl}(\text{bridging})$ distances are substantially longer with $\text{Ga}(1)-\text{Cl}(12) = 2.363(3)$ and $\text{Ga}(2)-\text{Cl}(12) = 2.369(3)\text{\AA}$ (average = $2.366 \pm 0.004\text{\AA}$); and the $\text{Ga}-\text{C}(\text{mesityl})$

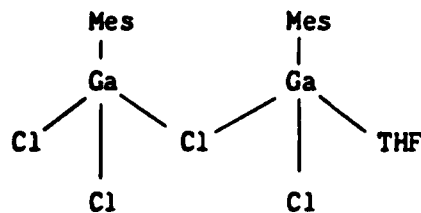
linkages are Ga(1)-C(11) = 1.970(14) and Ga(2)-C(21) = 1.943(12) Å (average = 1.957 ± 0.016 Å).

Each gallium(III) center has a rather distorted tetrahedral coordination environment. The smallest angles are those between the bridging chloride ligands [Cl(12)-Ga(1)-Cl(12)(x, 1/2-y, z) = 94.84(9)° and Cl(12)-Ga(2)-Cl(12)(x, -1/2-y, z) = 95.85(9)°] and the largest are those between the terminal chloride and mesityl ligands [Cl(1)-Ga(1)-C(11) = 130.67(34)° and Cl(2)-Ga(2)-C(21) = 133.56(29)°]. Intermediate values are observed for Cl(terminal)-Ga-Cl(bridging) [99.58(11)° and 99.02(11)°] and Cl(bridging)-Ga-C(mesityl) bond angles [112.88(34)° and 111.36(28)°]. The Ga(1)-Cl(12)-Ga(2) angle is 106.05(10)° as might be expected for a tetrahedral disposition of electron pairs about the bridging chloride ligand. All other distances and angles are in the normal range but of limited precision due to the rather poor quality of the crystals.

It is of interest to compare some average bond distances for [GaMesCl₂]_n with those for [Ga(C₅Me₅)Cl₂]₂, the only other compound of the general formula GaRCl₂ to be investigated by an X-ray structural study.¹¹ No major differences were noted. For the compounds [GaMesCl₂]_n and [Ga(C₅Me₅)Cl₂]₂, the average Ga-Cl(bridging) distances are 2.366 ± 0.004 Å and 2.362 ± 0.008 Å, whereas the average Ga-Cl (terminal) distances are 2.157 ± 0.010 Å and 2.124 ± 0.004 Å, respectively. The Ga-C(Mes) distance (1.957 ± 0.016 Å) is also similar to the Ga-C(C₅Me₅) distance¹¹ (1.97(1) Å).

The polymeric nature of GaMesCl₂ is likely to be responsible for its relatively high melting point, its insolubility in organic solvents and its reactivity pattern with a strong base such as THF. A comparison of these properties of GaMesCl₂ with those for some related organogallium halides which are believed to be dimeric¹⁸ suggests that [GaMesCl₂]_n is unique in

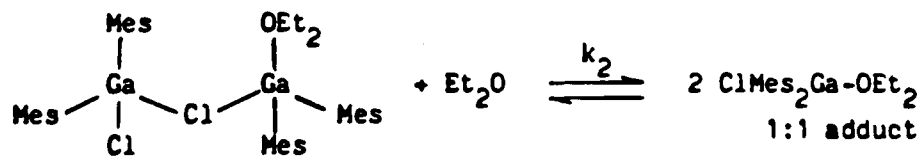
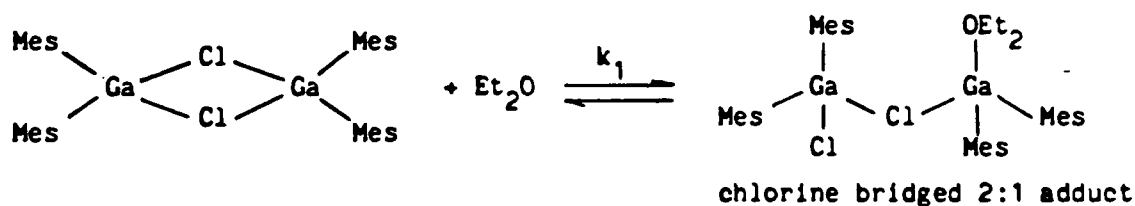
organogallium chemistry. It is noteworthy that a dimeric structure with bridging chloride atoms has been verified by X-ray structural studies for only two organogallium compounds,¹¹ $[\text{Ga}(\text{C}_5\text{Me}_5)_2\text{Cl}]_2$ and $[\text{Ga}(\text{C}_5\text{Me}_5)\text{Cl}_2]_2$, even though solution molecular weight and spectroscopic data are consistent with the proposed dimeric nature for a variety of other compounds.¹⁸ A comparison of melting point and solubility data for compounds in the series GaR_3 , GaR_2Cl and GaRCl_2 (Table IV) suggest that only GaMe_3Cl_2 has a unique polymeric structure. Only GaMe_3Cl_2 among organogallium dihalides has a melting point which is significantly higher than the corresponding diorganogallium halide. Similarly, only GaMe_3Cl_2 among the compounds listed in Table IV is insoluble in benzene, all others being soluble. It is also of interest to compare experimental observations when a base such as THF is added to organogallium halides mixed with benzene. The typical organogallium halide dissolved in benzene reacts rapidly with THF to form a solution of the simple 1:1 adduct. In contrast, when 0.136 mmol of GaMe_3Cl_2 dispersed in benzene was combined with 0.0680 mmol of THF at room temperature, no apparent reaction occurred over 18h. The off-white insoluble solid GaMe_3Cl_2 remained. However, after the mixture was heated in a 70°C oil bath for 15 min, all GaMe_3Cl_2 dissolved and a clear solution formed. The ^1H NMR spectrum of this solution revealed typical sharp lines at 2.48 (o-Me) and 2.04 (p-Me) but broadened lines for THF. These observations suggest that an adduct with the stoichiometry of the reaction mixture $(\text{GaMe}_3\text{Cl}_2)_2 \cdot \text{THF}$ had formed. The most likely structure for this unique adduct would incorporate a small unit of the polymer and would have one bridging chloride atom but all gallium atoms would be four coordinate.



It is unlikely that the solution contains a mixture of the 1:1 adduct ($\text{Cl}_2\text{MesGa}\cdot\text{THF}$) and excess GaMesCl_2 . For the 1:1 adduct to be formed, half of the available GaMesCl_2 would have to remain unreacted. The unreacted GaMesCl_2 would be expected to exist as a benzene insoluble solid. If new soluble forms of $[\text{GaMesCl}_2]_n$ were present, exchange reactions with $\text{Cl}_2\text{MesGa}\cdot\text{THF}$ would be expected. It is of interest that our NMR spectra of $\text{GaMes}_2\text{Cl}\text{-THF}$ and -OEt_2 solutions are also consistent with the formation of monochloride bridged 2:1 adducts (see the following discussion).

Monobridged 2:1 adducts have been previously described for some related aluminum^{21,23} and gallium^{22,23} compounds.

The ^1H NMR spectra (Figure 3) of solutions of GaMes_2Cl and Et_2O in benzene are consistent with equilibria between the dimer, the monochloride bridged 2:1 adduct and the simple 1:1 adduct as shown by the following equations. A solution of the dimer $(\text{GaMes}_2\text{Cl})_2$ in benzene with no added



ether exhibited a ^1H NMR spectrum with two lines in the methyl region, 2.40 (o-Me) and 2.07(p-Me)ppm (Figure 3a). After a small quantity of ether was added (0.24 mmol Et_2O /mmol GaMes_2Cl), four lines in the methyl region (2.44, 2.33, 2.14 and 2.07 ppm) were observed (Figure 3 b). The predominate lines correspond to $(\text{GaMes}_2\text{Cl})_2$. As the amount of ether was increased, the lines at 2.33 and 2.14 ppm increased in intensity relative to those of the dimer (Figure 3c). The lines at 2.33 and 2.14 ppm are therefore assigned to ortho-methyl and para-methyl groups of the chloride bridged 2:1 adduct. When the $\text{Et}_2\text{O}/\text{GaMes}_2\text{Cl}$ mol ratio was 0.58 or higher (Figures 3d,e,f), a new line at 2.57 ppm was evident and the relative integrations of the other four lines suggested that the line at 2.07 ppm arose from two components, the dimer and the 1:1 adduct. A high resolution spectrum of GaMes_2Cl with excess Et_2O in benzene revealed lines at 2.07 and 2.08 ppm in addition to the four other well resolved lines in the methyl region. Consequently, the lines at 2.57 (o-Me) and 2.08 (p-Me) ppm are assigned to the 1:1 adduct. The three species shown in the two equilibria should exhibit 6 methyl lines, provided the mesityl groups in the chloride bridged 2:1 adduct undergo rapid exchange. The number of observed lines and their intensities would eliminate the possibility of slow exchange for the chloride bridged 2:1 adduct or the presence of an ionic species such as $\text{Mes}_2\text{Ga}(\text{OEt}_2)_2^+$ $\text{GaMes}_2\text{Cl}_2^-$. It is noteworthy that when the $\text{Et}_2\text{O}/\text{GaMes}_2\text{Cl}$ mol ratio was 1.06 or higher, the species of highest concentration was the chloride bridged 2:1 adduct. This conclusion suggests that chlorine is a better base than Et_2O in this system. When Et_2O and benzene were removed by vacuum distillation, both adducts dissociated at room temperature and the dimer was reformed. When the stronger base THF was utilized, GaMes_2Cl formed an isolable 1:1 adduct. However, the ^1H NMR spectrum of a solution having a $\text{GaMes}_2\text{Cl}/\text{THF}$

mol ratio of one exhibited a minimum of five lines in the methyl region. The multiple lines in the methyl region would be consistent with the existence of the two equilibria as previously described for the Et₂O system. The derivative with only one bulky mesityl group GaMesCl₂ also reacts with THF to form an isolable 1:1 adduct. However, the ¹H NMR spectrum reveals only two lines in the methyl region, 2.57 (o-Me) and 2.11(p-Me), an observation consistent with the presence of only the 1:1 adduct.

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Supplementary Material Available. A table of anisotropic thermal parameters (page); a list of observed and calculated structure factor amplitudes (pages). Ordering information is given on any current masthead page.

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Table I

Experimental Data for the X-Ray Diffraction Study of Dichloromesitylgallium(III).

(A) Crystal Parameters at 24°C (297K)

crystal system: monoclinic

space group: $P2_1/m$ (C_{2h}^2 ; No. 11)

a = 8.3989(21)Å

b = 6.9976(19)Å

c = 18.0347(57)Å

β = 100.159(23)°

V = 1043.3(5)Å³

Z = 4 formula units

formula wt = 259.8 amu

ρ (calc'd) = 1.65 g cm⁻³

(B) Data Collection

diffractometer: Syntex P2₁

radiation: Mo K α (λ = 0.710730Å)

monochromator: highly oriented (pyrolytic) graphite, mounted in equatorial mode with $2\theta(m)$ = 12.160°; assumed to be 50% perfect/50% ideally imperfect for polarization correction.

reflections measured: $\pm h, \pm k, \pm l$ for 2θ = 5.0-45.0°; 2956 reflections measured and merged to 1502 point-group independent data: $R(I)$ = 5.7% for averaging 1250 pairs of reflections.

scan conditions: coupled θ (crystal)- 2θ (counter) from $[2\theta(K\alpha_1)-1.1]^\circ$ through $[2\theta(K\alpha_2)+1.1]^\circ$ at a scan speed of 4.0°/min in 2θ .

backgrounds: stationary crystal and counter at beginning and end of the 2θ scan; each for one-half of total scan time.

standard reflections: three (142, 52 $\bar{5}$, 411) collected after each batch of 97 reflections; no decay or instability detected.

absorption ($\mu = 32.3 \text{ cm}^{-1}$): corrected empirically by interpolation (in 2θ and ϕ) between ψ -scans of four close-to-axial reflections (30 $\bar{2}$ with $2\theta = 14.69^\circ$ and min/max = 0.710; 40 $\bar{1}$ with $2\theta = 24.51^\circ$ and min/max = 0.735; 60 $\bar{3}$ with $2\theta = 29.40^\circ$ and min/max = 0.713)

Table IIFinal positional parameters for Ga(C₆H₂Me₃)Cl₂^a

ATOM	X	Y	Z	BISO
GA(1)	0.49434(15)	0.25000(0)	0.29349(0)	
GA(2)	0.38263(15)	-0.25000(0)	0.22357(0)	
CL(1)	0.50000(43)	0.25000(0)	0.17474(20)	
CL(2)	0.64035(38)	-0.25000(0)	0.26564(23)	
CL(12)	0.30588(23)	0.00130(30)	0.29795(12)	
C(11)	0.6716(16)	0.25000(0)	0.38101(79)	
C(12)	0.6351(14)	0.25000(0)	0.45549(71)	
C(13)	0.7526(17)	0.25000(0)	0.51794(76)	
C(14)	0.9278(15)	0.25000(0)	0.50304(93)	
C(15)	0.9483(16)	0.25000(0)	0.4336(11)	
C(16)	0.8290(14)	0.25000(0)	0.37126(83)	
C(12A)	0.4541(15)	0.25000(0)	0.47165(81)	
C(14A)	1.0574(20)	0.25000(0)	0.5744(10)	
C(16A)	0.8725(15)	0.25000(0)	0.29188(84)	
C(21)	0.2528(13)	-0.25000(0)	0.12308(65)	
C(22)	0.3367(14)	-0.25000(0)	0.05672(75)	
C(23)	0.2445(15)	-0.25000(0)	-0.01389(73)	
C(24)	0.0609(16)	-0.25000(0)	-0.02179(79)	
C(25)	0.0025(17)	-0.25000(0)	0.0391(10)	
C(26)	0.0052(17)	-0.25000(0)	0.11385(77)	
C(22A)	0.5154(16)	-0.25000(0)	0.06566(89)	
C(24A)	-0.0434(20)	-0.25000(0)	-0.09872(93)	
C(26A)	-0.0079(13)	-0.25000(0)	0.17817(86)	
H(12A)	0.4558	0.2500	0.5254	6.0
H(12B)	0.3951	0.1391	0.4522	6.0

H(13)	0.7500	0.2500	0.5714	6.0
H(14A)	1.0100	0.2500	0.6194	6.0
H(14B)	1.1257	0.3600	0.5753	6.0
H(15)	1.0795	0.2500	0.4300	6.0
H(16A)	0.9845	0.2500	0.2937	6.0
H(16B)	0.8275	0.3600	0.2632	6.0
H(22A)	0.5800	-0.2500	0.0145	6.0
H(22B)	0.5551	-0.3600	0.0946	6.0
H(23)	0.2744	-0.2500	-0.0618	6.0
H(24A)	0.0203	-0.2500	-0.1368	6.0
H(24B)	-0.1119	-0.1391	-0.1037	6.0
H(25)	-0.0731	-0.2500	0.0754	6.0
H(26A)	0.0630	-0.2500	0.2337	6.0
H(26B)	-0.0761	-0.3600	0.1730	6.0

^a Hydrogen atoms are in idealized calculated positions; those of the methyl groups are based upon the locations of hydrogen atoms observed at $y = +1/4$ and $-1/4$.

Table III

Selected Interatomic Distances (Å) and Angles for Ga(C₆H₂Me₃)Cl₂.

(A) Distances involving the Gallium Atoms

Ga(1)···Ga(2)	3.781(1)	Ga(1)-Cl(1)	2.150(4)
Ga(1)···Ga(2)(x, 1+y, z)	3.781(1)	Ga(2)-Cl(2)	2.164(4)
Ga(2)···Ga(1)(x, -1+y, z)	3.781(1)	Ga(1)-C(11)	1.970(14)
Ga(1)-Cl(12)	2.363(3)	Ga(2)-C(21)	1.943(12)
Ga(1)-Cl(12)(x, 1/2-y, z)	2.363(3)		
Ga(2)-Cl(12)	2.369(3)		
Ga(2)-Cl(12)(x, -1/2-y, z)	2.369(3)		

(B) C-C (Ring) Distances within Mesityl Ligands

C(11)-C(12)	1.43(2)	C(21)-C(22)	1.49(2)
C(12)-C(13)	1.36(2)	C(22)-C(23)	1.37(2)
C(13)-C(14)	1.54(2)	C(23)-C(24)	1.52(2)
C(14)-C(15)	1.29(3)	C(24)-C(25)	1.28(3)
C(15)-C(16)	1.37(2)	C(25)-C(26)	1.40(2)
C(16)-C(11)	1.36(2)	C(26)-C(21)	1.39(2)

(C) C-Me Distances

C(12)-C(12A)	1.60(2)	C(22)-C(22A)	1.48(2)
C(14)-C(14A)	1.53(2)	C(24)-C(24A)	1.51(2)
C(16)-C(16A)	1.54(2)	C(26)-C(26A)	1.51(2)

(D) Angles Around the Gallium Atoms

Cl(1)-Ga(1)-Cl(12)	99.58(11)	Cl(2)-Ga(2)-Cl(12)	99.02(11)
Cl(1)-Ga(1)-Cl(12)(x, 1/2-y, z)	99.58(11)	Cl(2)-Ga(2)-Cl(12)(x, -1/2-y, z)	99.02(11)
Cl(1)-Ga(1)-C(11)	130.67(34)	Cl(2)-Ga(2)-C(21)	133.56(29)
Cl(12)-Ga(1)-Cl(12)(x, 1/2-y, z)	94.84(9)	Cl(12)-Ga(2)-Cl(12)(x, -1/2-y, z)	95.85(9)
Cl(12)-Ga(1)-C(11)	112.88(34)	Cl(12)-Ga(2)-C(21)	111.36(28)
C(11)-Ga(1)-Cl(12)(x, 1/2-y, z)	112.88(34)	C(11)-Ga(2)-Cl(12)(x, -1/2-y, z)	111.36(28)

(E) Angle at Bridging Chloride Ligand

Ga(1)-Cl(12)-Ga(2) = 106.05(10)

Table IV

Comparison of Melting Points (°C) of Aryl Gallium Compounds.

<u>Compound/R(X)</u>	<u>Mes(Cl)</u>	<u>C₆H₅(Cl)</u>	<u>C₆H₅(Br)</u>	<u>C₆H₅(I)</u>
GaR ₃	186-187.8 ^a	166 ^b	166 ^b	166 ^b
GaR ₂ X	158-159.5	194-196 ^c	223-225 ^c	191-192 ^c
GaRX ₂	199-201.5	122-123 ^c	134-135 ^c	86-87 ^c

a. Reference 8

b. Reference 19

c. Reference 20

Captions to Figures

Figure 1. The polymeric structure of dichloromesitylgallium(III). [The b-axis is horizontal with a repeat distance of 6.998(2)Å.] The angles Ga(2)···Ga(1)···Ga(2) (x, 1+y, z) and Ga(1)···Ga(2)···Ga(1) (x, -1+y, z), which define the kink in the zig-zag polymer, are equivalent at 135.46(4)°.

Figure 2. The crystallographic asymmetric unit of dichloromesitylgallium(III) with atomic labelling. The view is perpendicular to that of Figure 1 and the structure extends by Ga(2) linking to a further symmetry related bridging chloride ligand above the position of Cl(12) and by Ga(1) linking to a further bridging chloride ligand below the position of Cl(12).

Figure 3. The 90 MHz ¹H-NMR spectra (δ ppm) of GaMes₂Cl in benzene solution with increasing concentrations of diethyl ether given in mmol Et₂O/mmol GaMes₂Cl (top left to bottom right).

FIG. 1

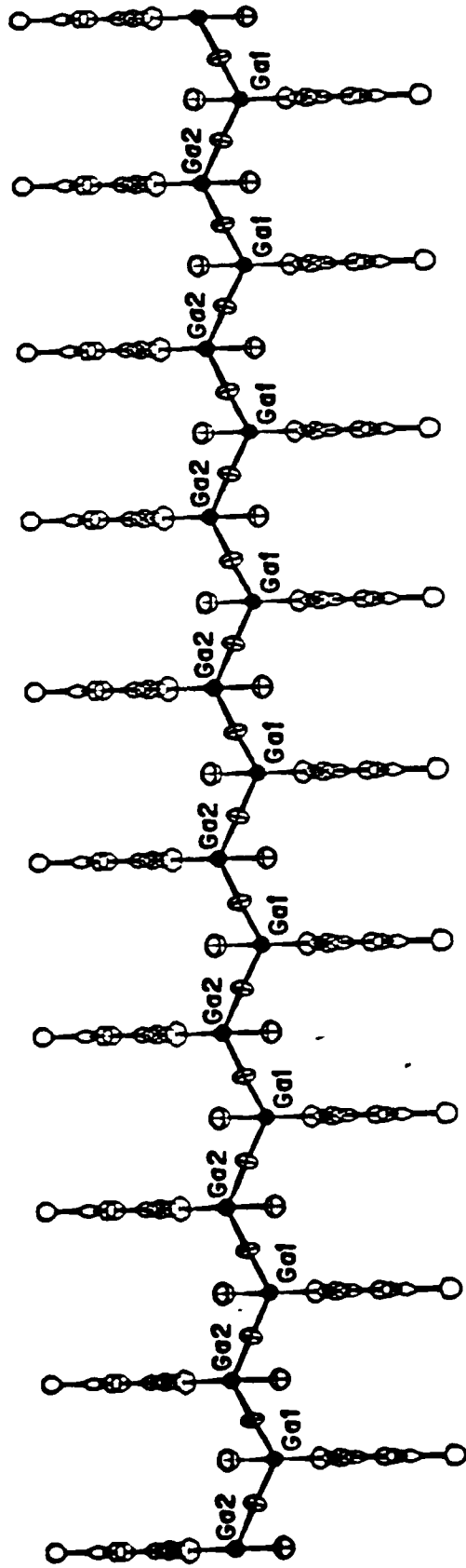
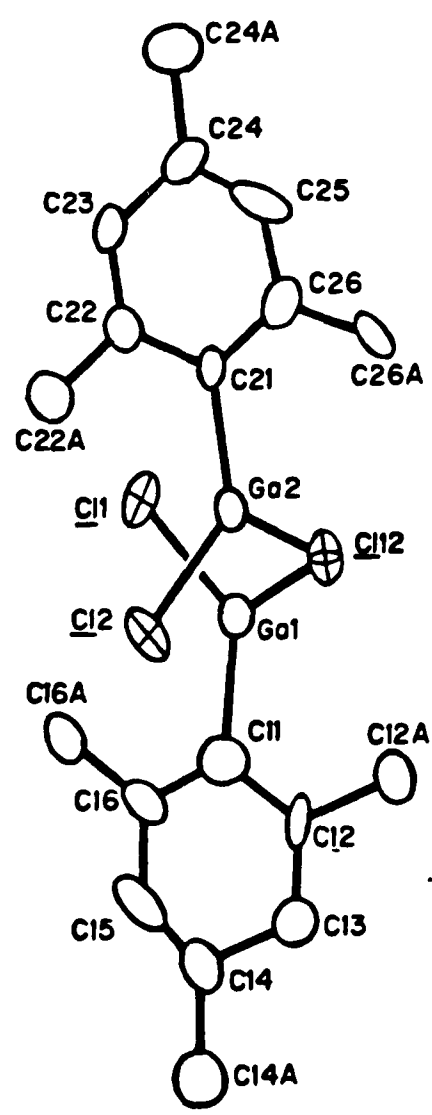
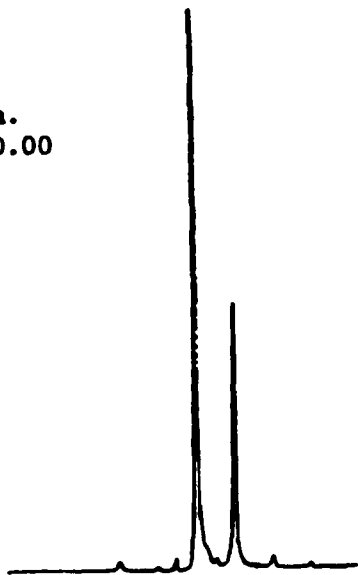


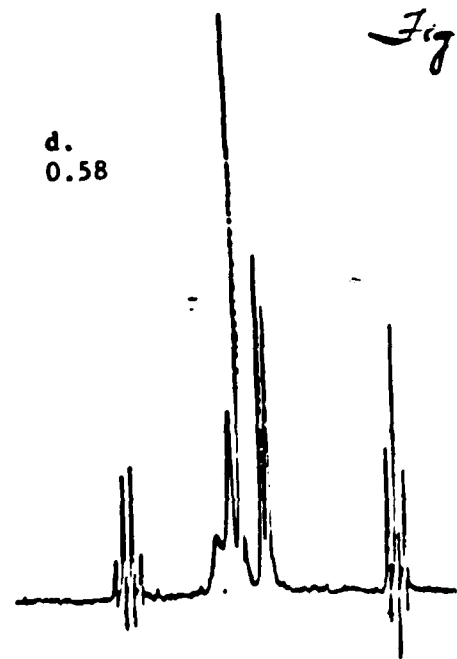
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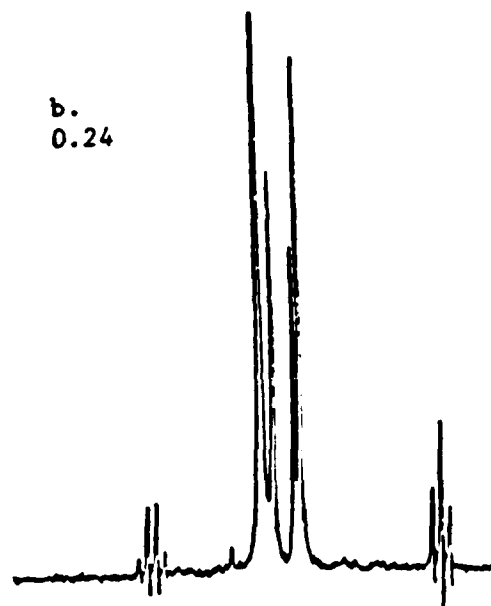
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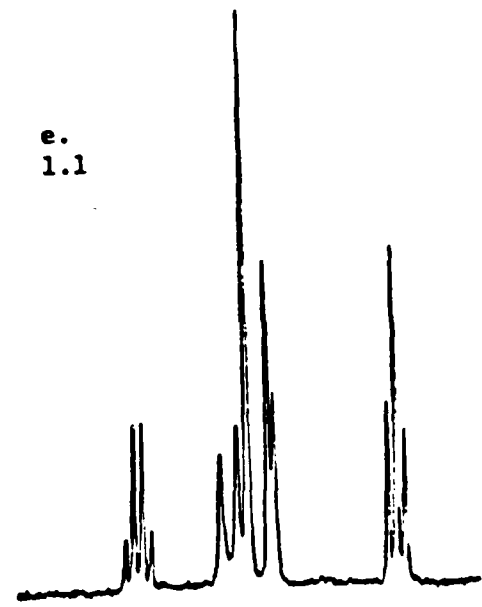
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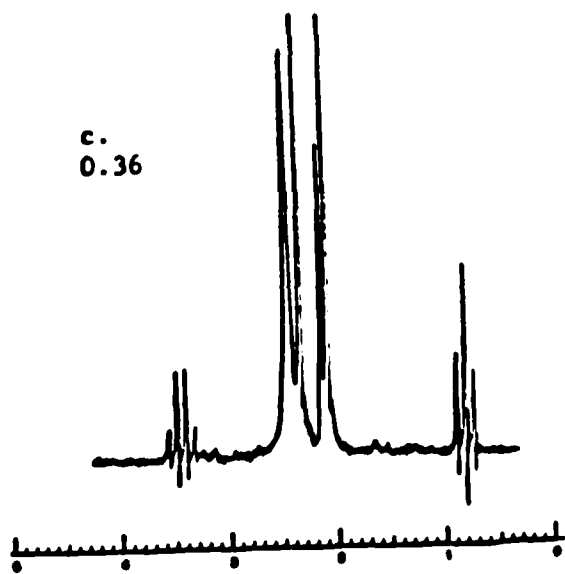
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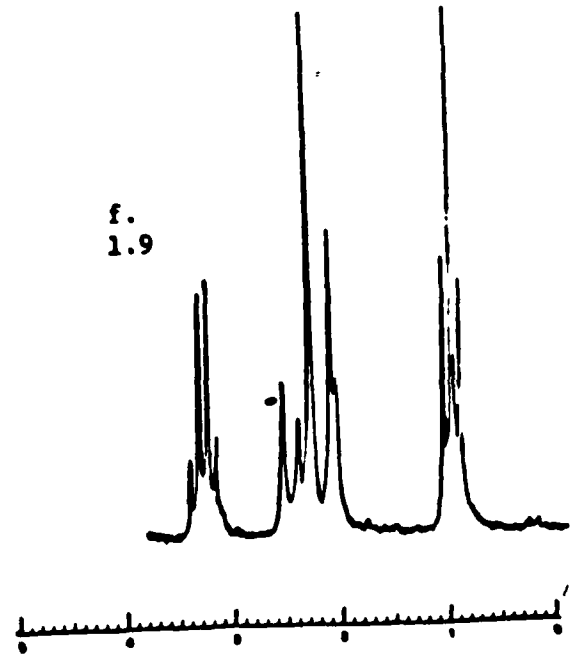
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