sample sealed in a 3-mm. tube under nitrogen. The solutions used for the measurement of the spectrum of $(NH_4)_2[MoOCl_5]$ were 0.03 *M*. It was noted that the line width of this compound does not change on dilution to 0.003 *M*, therefore the more concentrated solution was chosen to obtain a stronger signal. The strength of a given line was measured by the area under the curve. All e.s.r. measurements were made at 19 ± 1°. The magnetic susceptibility measurements of Sacconi and Cini[5] on MoO^{3+} solutions were made at 20°.

(3) **Magnetic Susceptibilities.**—The magnetic susceptibility measurements were carried out on a Gouy balance using an electromagnet with a maximum field strength of about 3000 gauss. The balance was fitted with a suitable dewar flask to contain the cooling liquids. Temperatures between 77 and 273°K. were achieved by using precooled isopentane and allowing it to warm up slowly.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE
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The Structure of the Diammoniate of Dimethylgallium Chloride, $(CH_3)_2ClGa\cdot 2NH_3$, and of Ethylenediamine–Dimethylgallium Chloride

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Chemical evidence supports the structure $[(CH_3)_2Ga(NH_3)_2]Cl$ for the known compound $(CH_3)_2GaCl\cdot 2NH_3$ reported by Kraus and Toonder and the structure $[(CH_3)_2Ga(H_2NCH_2CH_2NH_2)]Cl$ for the new ethylenediamine analog. The latter compound is stable in water for limited periods of time.

The compound $(CH_3)_2GaCl\cdot 2NH_3$ was reported by Kraus and Toonder[1] in 1933, but the structure was never established. An ammonium model, analogous to the early ammonia model used for the diammoniate of diborane, was suggested by Coates[2]: $[NH_4^+][(CH_3)_2GaNH_2Cl^-]$; however, little real structural evidence was ever available. Following recognition of the formula $[H_2B(NH_3)_2][BH_4]$ for the diammoniate of diborane,[3] another possible structure for the diammoniate of dimethylgallium chloride appeared probable: $[(CH_3)_2Ga(NH_3)_2]Cl$. Chemical evidence supports this latter model.

Experimental

General Procedures.—Standard vacuum line techniques were used with moisture- and oxygen-sensitive materials.[4] Filtration of air-sensitive materials was performed with the vacuum line filtration assembly which is described elsewhere.[5]

X-Ray powder patterns were obtained in 5.7 and 11.4 cm. diameter cameras with CuKα radiation. Films were read on a North American Philips film reader and intensities were estimated visually. Infrared spectra were obtained on a Perkin-Elmer Model 21 double beam recording spectrophotometer with NaCl optics; KCl disk and Nujol mull techniques were employed. Calibration of the spectrometer was checked with indene.[6]

Materials. 1. $Ga(CH_3)_3$ was prepared by the action of 67.8 g. of $Hg(CH_3)_2$ on 13.22 g. of Ga metal (99.99% pure) in the presence of a trace of mercuric chloride. Reaction took place in a sealed glass pressure tube at 130° over a period of 9 days.[7] The $Hg(CH_3)_2$ was prepared by the method of Marvel and Gould.[8] Three fractionations of the crude $Ga(CH_3)_3$ from a vacuum trap at room temperature, through a trap at 0°, and into a trap at −78° gave a product with a vapor pressure of 65.4 mm. at 0°. This compares well with the literature values of 66.6,[7] 64.5,[9] and 65.9 mm.[1] The yield was nearly quanti-

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[1] C. A. Kraus and F. E. Toonder, *Proc. Natl. Acad. Sci. U. S.*, **19**, 292 (1933).

[2] G. E. Coates, "Organo Metallic Compounds," Methuen and Co., Ltd., John Wiley and Sons, Inc., New York, N. Y., 1960, p. 147.

[3] S. G. Shore, D. R. Schultz, R. W. Parry, *et al.*, *J. Am. Chem. Soc.*, **80**, 1–29 (1958).

[4] R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, New York, N. Y., 1948.

[5] R. W. Parry, D. R. Schultz, and P. R. Girardot, *J. Am. Chem. Soc.*, **80**, 2 (1958).

[6] R. N. Jones, P. K. Faure, and W. Zaharias, *Rev. Universelle Mines*, **15**, 417 (1959).

[7] E. Wiberg, T. Johannsen, and O. Stecher, *Z. anorg. Chem.*, **251**, 114 (1943).

[8] C. S. Marvel and V. L. Gould, *J. Am. Chem. Soc.*, **44**, 153 (1922).

[9] T. Wartik and H. I. Schlesinger, *ibid.*, **75**, 835 (1953).

tative.

2. HCl (Matheson, anhydrous) was fractionated from a trap at −112° before use.

3. NH_3 (Matheson, anhydrous) was stored over sodium and distilled from Na before use.

4. $H_2NCH_2CH_2NH_2$ (98% Eastman ethylenediamine) was refluxed over Na for about 3 hr. and then fractionally distilled (b.p. = 112.9–113.0° uncor.) onto dried and outgassed Linde Molecular Sieves (5A). The base was stored over the sieves in a closed container. Prior to use it was sublimed from a trap at 0° into a trap held at −78°.

5. KBH_4 (Metal Hydrides, Inc.) was crystallized from liquid ammonia before use.

The Preparation and Reactions of $Ga(CH_3)_2Cl \cdot 2NH_3$. 1. The Preparation of $(CH_3)_2GaCl \cdot 2NH_3$.—The method of Kraus and Toonder[1] (*i.e.*, the addition of HCl to $(CH_3)_3GaNH_3$ followed by the addition of NH_3) was slow and the product was contaminated with NH_4Cl. A more satisfactory procedure was based on the reactions

$$(CH_3)_3Ga + HCl \xrightarrow{(C_2H_5)_2O} (CH_3)_2GaCl + CH_4 \quad (1)$$

$$(CH_3)_2GaCl + 2NH_3 \longrightarrow (CH_3)_2GaCl \cdot 2NH_3 \quad (2)$$

In a typical run a 0.656 mmole sample of HCl was distilled onto an equimolar quantity of $Ga(CH_3)_3$ in 5 ml. of *n*-hexane. A volume of CH_4 amounting to 0.648 mole was collected (mol. wt. obsd. 15.1; 98.9% of theory for reaction 1) (ref. 2, p. 151). The resulting $(CH_3)_2GaCl$ absorbed 1.315 mmoles of NH_3 (100% of theory for reaction 2) to give a precipitate of $(CH_3)_2GaCl \cdot 2NH_3$ which was filtered from the hexane in the vacuum line filtration assembly. The product was washed twice with ethyl ether, and then dissolved in NH_3 and filtered. The excess solvent was pumped off and the dry crystals were manipulated in a nitrogen filled drybox into X-ray capillaries, reaction assemblies, or infrared pellets. Samples of the solid product melted from 110–113°. Kraus and Toonder reported a melting point of 112°. The X-ray powder pattern (Table I) was identical with the product prepared by the procedure of Kraus and Toonder. The empirical formula, $(CH_3)_2GaCl \cdot 2NH_3$, was confirmed by analysis. (C, H, N, and Cl were determined by Spang Microanalytical Laboratory, Ann Arbor, Michigan.) *Anal.* Calcd. for $(CH_3)_2GaCl \cdot 2NH_3$: C, 14.19; H, 7.14; N, 16.55; Cl, 20.94; Ga, 41.18. Found: C, 14.26; H, 7.02; N, 16.49; Cl, 21.06; Ga, 40.90. Gallium was determined by hydrolyzing the sample in 6 *M* H_2SO_4, drying under an infrared lamp, igniting, and weighing as Ga_2O_3. The molecular weight of $(CH_3)_2GaCl \cdot 2NH_3$ was determined by the vapor pressure depression of its liquid NH_3 solution. Extrapolation of the linear portion of the molecular weight–concentration curve gave a value of 174 at infinite dilution. This compares with a theoretical value of 169 expected for the salt $[(CH_3)_2Ga(NH_3)_2]Cl$ composed of ion pairs.[13]

TABLE I

INTERPLANAR SPACINGS AND RELATIVE INTENSITIES FROM X-RAY POWDER PATTERNS

$[(CH_3)_2Ga(NH_3)_2{}^+]Cl^-$		$[(CH_3)_2Ga(NH_3)_2]BH_4$ ammonia soluble metathesis product	
Intensity	d (Å.)[b]	Intensity	d (Å.)[a]
w	8.14	vvw	7.37
s	6.48	s	5.82
s	5.00	vs	5.36
w	4.16	s	4.96
m	3.94	s	4.69
m	3.73	mw	4.45
w	3.37	w	4.16
m	3.25	w	3.80
m	3.15	w	3.59
m	3.00	mw	3.28
m	2.65	vs	3.14
w	2.50	w	2.82
vw	2.44	w	2.63
vw	2.21	w	2.48
vw	2.08	mw	2.32
w	2.04	m	2.23
vw	1.97	m	2.00
vw	1.89		
m	1.79		
m	1.75		

v, very; s, strong; m, medium; w, weak.

[a] These data were collected with a 57 mm. diameter powder camera. [b] Lines due to NH_4Cl have been subtracted from these data.

2. The Thermal Decomposition of $(CH_3)_2GaCl \cdot 2NH_3$.—When solid $(CH_3)_2GaCl \cdot 2NH_3$ was allowed to stand at room temperature, the powder pattern of the sample slowly changed from that of the original substance to that of NH_4Cl plus some substance giving diffuse scattering. This transformation occurred without the evolution of gas, and, judging from the powder pattern, it was complete in two weeks at room temperature. A slightly volatile decomposition product was separated from the NH_4Cl. A low-resolution mass spectrum of this product showed a parent peak at 230 ± 4, which is consistent with the presence of $[(CH_3)_2GaNH_2]_2$ (molecular weight 231.6) previously reported by Coates.[11] On the basis of this evidence the decomposition equation is

$$2[(CH_3)_2Ga(NH_3)_2]Cl \longrightarrow [(CH_3)_2GaNH_2]_2 + 2NH_4Cl$$

but the presence of some dimethylgallium amide in other degrees of polymerization cannot be ruled out.

3. Chloride Displacement Reactions by Metathesis of $[(CH_3)_2Ga(NH_3)_2]Cl$.—Because of the water sensitivity of $[(CH_3)_2Ga(NH_3)_2]Cl$, metathesis reactions were conducted in liquid ammonia. The following reaction with KBH_4 was expected

$$KBH_4 + [(CH_3)_2Ga(NH_3)_2]Cl \longrightarrow KCl\downarrow + [(CH_3)_2Ga(NH_3)_2]BH_4$$

In a typical reaction 0.250 mmole of KBH_4 and 0.190 mmole of $[(CH_3)_2Ga(NH_3)_2]Cl$ were stirred in the vacuum filtration assembly with about 3 ml. of liquid NH_3. The KCl precipitate which formed was filtered off and identified by the powder pattern. The solid obtained by evaporating NH_3 from the filtrate decomposed slowly on standing at room temperature, evolving a non-condensable gas, presumably H_2 (0.003 mmole in 20 min.). The X-ray powder pattern of this solid, shown in Table I, changed slowly on

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(10) R. W. Parry, G. Kodama, and D. R. Schultz, *J. Am. Chem. Soc.*, **80**, 24 (1958).

(11) G. E. Coates, *J. Chem. Soc.*, 2003 (1951).

TABLE II

INTERPLANAR SPACINGS AND RELATIVE INTENSITIES OF $[(CH_3)_2Ga(en)]Cl$

Intensity	d (Å.)	Intensity	d (Å.)
w	7.03	w	2.16
vw	6.05	w	2.11
s	5.48	w	2.06
s	5.04	w	2.01
s	4.34	w	1.97
s	4.21	m	1.88
m	3.62	w	1.83
w	3.50	m	1.78
s	3.24	w	1.75
w	3.15	m	1.67
w	3.02	w	1.65
w	2.95	w	1.60
m	2.75	m	1.58
w	2.53	w	1.55
m	2.46	vw	1.52
m	2.40	w	1.49
vw	2.34	vw	1.44
vw	2.28	w	1.40
m	2.20	w	1.36

v, very; s, strong; m, medium; w, weak.

TABLE III

INFRARED DATA FOR $[(CH_3)_2Ga(en)]Cl$ AND $[(CH_3)_2Ga(en)]_2SO_4$[a]

$[(CH_3)_2Ga(en)]_2SO_4$ cm.$^{-1}$	$[(CH_3)_2Ga(en)]Cl$ cm.$^{-1}$
3385–3260 (broad sh.) s	*ca.* 3430 (sh.) m
	3365 (max.) m
3130–3050 (broad sh.) s	3125 (max.) s
	3160 (sh.) s
ca. 2920 (sh.) m	*ca.* 2930 (sh.) m
1630–1596 (broad max.) m	1598 (max.) m
1536 (max.) m	
1458 (max.) m	1457 (max.) m
1367 (max.) w	1367 (max.) w
1344 (sh.) mw	
1335 (max.) mw	1334 (max.) mw
1313 (max.) w	1313 (max.) mw
1286 (max.) w	1287 (max.) mw
1217 (max.) vw	1217 (max.) m
1180 (max.) vw	1181 (max.) w
1138 (max.) m	1140 (max.) ms
1082 (broad max.) m	
1054 (max.) m	1055 (max.) s
1016 (max.) w	1016 (max.) mw
794 (max.) mw	799 (max.) mw
740 (max.) m	744 (max.) m

v, very; s, strong; m, medium; w, weak; sh., shoulder; max., maximum.

[a] All data were obtained in KCl disks; however, spectra of Nujol mulls were substantially the same.

standing at 20–25°. No lines for H_3NBH_3 appeared in the pattern of the decomposed product. Analysis of the ammonia-soluble product, presumed to be $[(CH_3)_2Ga(NH_3)_2]BH_4$, was not attempted because of instability. Infrared spectra of the product in KCl disks were those of the decompostion product. The existence of a separate new phase which decomposed on standing gave evidence for the expected unstable $[(CH_3)_2Ga(NH_3)_2]BH_4$.

The Preparation and Reactions of $[(CH_3)_2Ga(H_2NCH_2CH_2NH_2)]Cl$—Base Displacement Reactions of $[(CH_3)_2Ga(NH_3)_2]Cl$. 1. Preparation of $[(CH_3)_2Ga(H_2NCH_2CH_2NH_2)]Cl$.—Because of its greater tendency to form stable coördination compounds, ethylenediamine ($H_2NCH_2CH_2NH_2$ = en) might be expected to replace NH_3 from $(CH_3)_2GaCl\cdot 2NH_3$ in a base displacement reaction. The expected equation is

$$[(CH_3)_2Ga(NH_3)_2]Cl + en \longrightarrow [(CH_3)_2Ga(en)]Cl + 2NH_3$$

In a typical run a 0.184 mmole sample of $[(CH_3)_2Ga(NH_3)_2]Cl$ was dissolved in an excess of ethylenediamine; a 0.360 mmole sample of NH_3 was liberated (98% of theory for the equation given above). Excess ethylenediamine was removed under vacuum, and the solid was washed twice with diethyl ether to give a stable white solid. *Anal.* Calcd. for $[(CH_3)_2Ga(H_2NCH_2CH_2NH_2)]Cl$: C, 24.59; H, 7.22; N, 14.34; Ga, 35.70; Cl, 18.15. Found: C, 25.25; H, 6.91; N, 14.42; Ga, 35.23; Cl, 18.72.

An identical product was also produced by the direct action of en on $(CH_3)_2GaCl$ in dimethyl ether. The equations are

$$(CH_3)_3Ga + HCl \xrightarrow{(CH_3)_2O} (CH_3)_2GaCl + CH_4$$

$$(CH_3)_2GaCl + en \longrightarrow (CH_3)_2GaCl\cdot en$$

In a typical reaction a 2.2 mmole sample of $(CH_3)_3Ga$ in 5 ml. of dimethyl ether was mixed with an equimolar quantity of HCl in the vacuum system and the resulting CH_4 was pumped off. Approximately half of the ether was removed and an excess of ethylenediamine was distilled into the reaction tube. The white precipitate which formed was filtered off in the vacuum filtration assembly, washed three times with fresh ether, and dried under high vacuum at about 25°. The resulting white solid gave an X-ray powder pattern (Table II) which was identical to that of the product produced by displacement of NH_3 from $[(CH_3)_2Ga(NH_3)_2]Cl$. Infrared spectra (Table III) and analysis also established the identity of the two samples.

The product $[(CH_3)_2Ga(en)]Cl$ is a stable white solid which does not melt below 130°; it is insoluble in diethyl ether, but soluble in ethylenediamine, water, and ethyl alcohol. In the latter two solvents it is stable for short periods of time but decomposes on prolonged standing. For example, molecular weight measurements of $[(CH_3)_2Ga(en)]Cl$ in water at *ca.* 0° showed no consistent variation over a period of 1 hr. Another aqueous solution of $[(CH_3)_3Ga(en)]Cl$ was allowed to stand at 25° for 3 min. and then evaporated under vacuum. The X-ray powder pattern and infrared spectrum of the solid which remained were identical with those of $[(CH_3)_2Ga(en)]Cl$.

The molecular weight of $[(CH_3)_2Ga(en)]Cl$ was determined in water solution by freezing point depression. An average value of 90 ± 3[12] was obtained as a result of six separate measurements; the value expected for $[(CH_3)_2Ga(en)]Cl$ with two ions per formula weight is 97.

2. Metathesis Reactions of $[(CH_3)_2Ga(en)]Cl$ and Derivatives.—If one assumes the foregoing formula for

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[12] This limit of error represents the standard deviation.

$[(CH_3)_2Ga(en)]Cl$, the reaction of the ethylenediamine complex with Ag_2SO_4 in water should be

$$2[(CH_3)_2Ga(en)]Cl + Ag_2SO_4 \longrightarrow 2AgCl\downarrow + [(CH_3)_2Ga(en)]_2SO_4$$

A 0.10 mmole sample of $[(CH_3)_2Ga(en)]Cl$ was dissolved in 3 ml. of a 50/50 water–ethanol solvent mixture and an approximately equimolar quantity of Ag_2SO_4 in a saturated aqueous solution was added. The precipitate of AgCl which formed rapidly was filtered off and excess solvent vaporized under vacuum. The solid which remained gave a unique X-ray powder pattern (Table II) and a characteristic infrared spectrum (Table III).

The sulfate salt could be reconverted to the chloride salt by the process

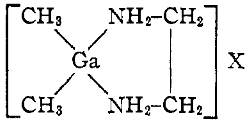
$$[(CH_3)_2Ga(en)]_2SO_4 + BaCl_2 \longrightarrow BaSO_4 + 2[(CH_3)_2Ga(en)]Cl$$

A 0.02 mmole sample of $[(CH_3)_2Ga(en)]_2SO_4$ in 3 ml. of water was treated with an approximately equimolar quantity of aqueous $BaCl_2$ solution. The $BaSO_4$ was filtered off; solvent was evaporated from the filtrate under vacuum and a solid product remained. An X-ray powder pattern for this solid was identical with the original pattern for $[(CH_3)_2Ga(en)]Cl$.

Discussion

Strong evidence is provided for representing $(CH_3)_2GaCl\cdot en$ by the ionic formula $[(CH_3)_2Ga(en)]Cl$. The following facts are pertinent. (1) The elemental analysis establishes the empirical formula as $(CH_3)_2GaCl\cdot en$. (2) The molecular weight of the compound, as determined by freezing point depression in water solution, is 90, as compared with a theoretical value of 97 expected for an ionic structure containing two ions per formula weight. (3) Conversion of the chloride salt to the corresponding sulfate by metathesis has been achieved: $2[(CH_3)_2Ga(en)]Cl + Ag_2SO_4 \rightarrow [(CH_3)_2Ga(en)]_2SO_4 + 2AgCl\downarrow$ and the sulfate also has been reconverted to the chloride by metathesis: $[(CH_3)_2Ga(en)]_2SO_4 + BaCl_2 \rightarrow 2[(CH_3)_2Ga(en)]Cl + BaSO_4\downarrow$. (4) An analysis of the infrared spectra of the salts provides additional support for the model. The spectrum of $[(CH_3)_2Ga(en)]_2SO_4$ in Table III is the same as that of $[(CH_3)_2Ga(en)]Cl$ except for the addition of a peak for the sulfate anion at 1082 cm.$^{-1}$. K_2SO_4 shows a peak at 1110 cm.$^{-1}$. The infrared spectrum also indicates that the $SO_4^=$ is not coördinated directly to the gallium in a bridge structure. Bertin, Penland, Mizushima, Curran, and Quagliano[13] report that the sulfate infrared absorption frequencies in $[Co(NH_3)_5SO_4]Cl$ occur at 1278, 1137, 1045, and 975 cm.$^{-1}$, as opposed to a single broad sulfate band in K_2SO_4 at 1110 cm.$^{-1}$. The origin of these new frequencies is apparently the loss of degeneracy when a tetrahedral sulfate ion is placed in a field of low symmetry which occurs in the first coördination sphere of the complex cation. The *single* sulfate infrared band in $[(CH_3)_2Ga(en)]_2SO_4$ at 1082 cm.$^{-1}$ indicates that sulfate is not directly coördinated to gallium.

The only obvious structure which is consistent with all of the foregoing facts is



Although no direct experimental evidence is available, a tetrahedral distribution of ligands around Ga^{+3} is expected.

Arguments supporting the ionic model for $(CH_3)_2GaCl\cdot 2NH_3$ are somewhat less direct than those for the ethylenediamine complex, but are still convincing. (1) Analogy with the ethylenediamine complex is close and suggests a similar structure. The ethylenediamine adduct and ammonia adduct are prepared by a common type reaction and ethylenediamine can replace ammonia from the ammonia adduct to give $[(CH_3)_2Ga(en)]Cl$. (2) The molecular weight of $[(CH_3)_2Ga(NH_3)_2]Cl$ in liquid NH_3 corresponds to one formula weight which is the value expected for this ion pair. (3) A metathesis reaction with KBH_4 in liquid ammonia produced KCl and a new product presumed to be $[(CH_3)_2Ga(NH_3)_2]BH_4$. The borohydride salt decomposes slowly, as expected, but the rate of decomposition is much slower than that observed for NH_4BH_4. This fact argues against any model containing the NH_4^+ ion and BH_4^- ion together. (4) The spontaneous decomposition of $[(CH_3)_2Ga(NH_3)_2]Cl$ to NH_4Cl and $[(CH_3)_2Ga(NH_2)]_2$ is also consistent with the above model but less so with any other.

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(13) E. P. Bertin, R. B. Penland, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **81**, 3818 (1959).