330. *Addition Compounds of Gallium Trichloride. Part V.*[1] *Ionic 1 : 1 and 1 : 2 Complexes with Pyridine.*

By N. N. Greenwood and K. Wade.

The new compounds $GaCl_3,C_5H_5N$ (m. p. 126°) and $GaCl_3,2C_5H_5N$ (m. p. 113°) have been established by phase studies on the system gallium trichloride–pyridine. The 1 : 1 complex distils unchanged at low pressures but the 1 : 2 complex loses pyridine readily under these conditions. Both complexes form ionic melts and their conductivity, viscosity, density, and surface tension have been determined over a range of temperatures. The vapour pressure of the 1 : 1 complex has also been studied. These properties are compared with those of related complexes and arguments are presented which suggest that the structures of the complexes are $[(C_5H_5N)_2GaCl_2]^+GaCl_4^-$ and $[(C_5H_5N)_2GaCl_2]^+Cl^-$.

When pyridine is distilled in vacuum on to gallium trichloride there is a rapid exothermic reaction which yields either a 1 : 1 or 1 : 2 co-ordination compound, depending on the molar ratio of the reactants. The 1 : 1 compound is the more stable but both can be investigated by means of the techniques described earlier.[1] There is no evidence for a 1 : 3 compound such as has been reported for indium trichloride,[2] thallium trichloride,[3,4] and thallium tribromide [4] with pyridine.

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[1] Part IV, Greenwood, Perkins, and Wade, *J.*, 1957, 4345.

[2] Renz, *Z. anorg. Chem.*, 1903, **36**, 101.

[3] Meyer, *ibid.*, 1900, **24**, 321; Renz, *Ber.*, 1902, **35**, 1110.

[4] Abbott, *Iowa State Coll. J. Sci.*, 1943, **18**, 3.

The specific electrical conductivity, viscosity, density, and surface tension of the 1 : 1 and the 1 : 2 complex, as well as the vapour pressure of the 1 : 1 complex have been determined over a range of temperature and from these have been derived the molar conductivity, reduced conductivity, activation energies of conduction and viscous flow, surface free energy, Eötvös constant, parachor, and heat of evaporation. Both complexes dissociate considerably into ions but an unequivocal assignment of structure was not possible since electrolysis of the melt resulted in an irreversible charring process at the anode, no reaction being visible at the cathode. However, comparison of the results with those obtained on related complexes favours the suggestion that the 1 : 1 compound is dipyridinedichlorogallium tetrachlorogallate $[py_2GaCl_2]^+GaCl_4^-$, the 1 : 2 compound being either the corresponding chloride $[py_2GaCl_2]^+Cl^-$ or the tetrachlorogallate $[py_4GaCl_2]^+GaCl_4^-$.

EXPERIMENTAL AND RESULTS

Gallium trichloride, m. p. 77·8°, was prepared, purified, and handled as described in Part I.[5] Pyridine, m. p. −41°, b. p. 115·3°, was dried by refluxing it for several hours over potassium hydroxide or barium oxide and then fractionating it in a 60 cm. column packed with glass helices. It was subsequently handled in a vacuum line. The methods used to measure the electrical conductivity,[6,7] viscosity,[8,9] density, and surface tension[9] have been described earlier.

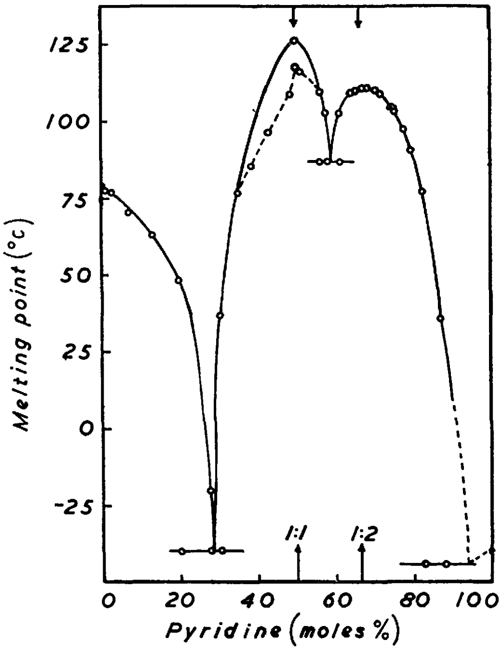

FIG. 1. *Phase diagram of the system* $GaCl_3$–C_5H_5N.

The vapour pressure of gallium trichloride–pyridine was obtained by sealing the complex into a side limb attached to a U-tube 8 mm. in diameter containing mercury. The mercury was degassed by heating it to 200—250° under dynamic vacuum before sealing off both arms of the manometer; the complex was likewise degassed by melting it under dynamic vacuum. The whole apparatus was then immersed in a thermostatted oil bath in a transparent Dewar vessel. Differences in levels were read on a cathetometer to ±0·02 mm. and corrected for thermal expansion of the mercury.

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[5] Greenwood and Wade, *J.*, 1956, 1527.
[6] Greenwood and Worrall, *J. Inorg. Nuclear Chem.*, 1957, **3**, 357.
[7] Greenwood and Wade, *J.*, 1957, 1516.
[8] *Idem, J. Sci. Instrum.*, 1957, **34**, 288.
[9] *Idem, J. Inorg. Nuclear Chem.*, 1957, **3**, 349.

Results.—The m. p. diagram of the system gallium trichloride–pyridine is shown in Fig. 1. There are well-defined maxima at 50·0 and 66·7 moles % of pyridine and eutectics at 28·5% (−40°), 59·0% (86°), and 93% (−45°). The 1 : 1 compound melted at 119° when prepared during these phase studies because of slight decomposition or the presence of impurities introduced during the successive addition or removal of weighed amounts of pyridine from the vacuum line. Direct preparations when purified by fractional freezing melted at 126°.

The flatter maximum of the 1 : 2 complex at 113° indicates that this compound is more dissociated in the liquid phase than is the 1 : 1 complex. This is consistent with the fact that gallium trichloride absorbs pyridine with considerable evolution of heat up to the equimolar ratio but beyond this pyridine must be added by cooling the reaction mixture in a bath of ethanol–solid carbon dioxide. Pyridine in excess of the 1 : 1 ratio could always be removed from the molten mixture by vacuum distillation and this afforded an alternative means of preparing the pure 1 : 1 compound which could itself be sublimed or distilled *in vacuo* without decomposition.

FIG. 2. *Properties of molten* $GaCl_3,C_5H_5N$.

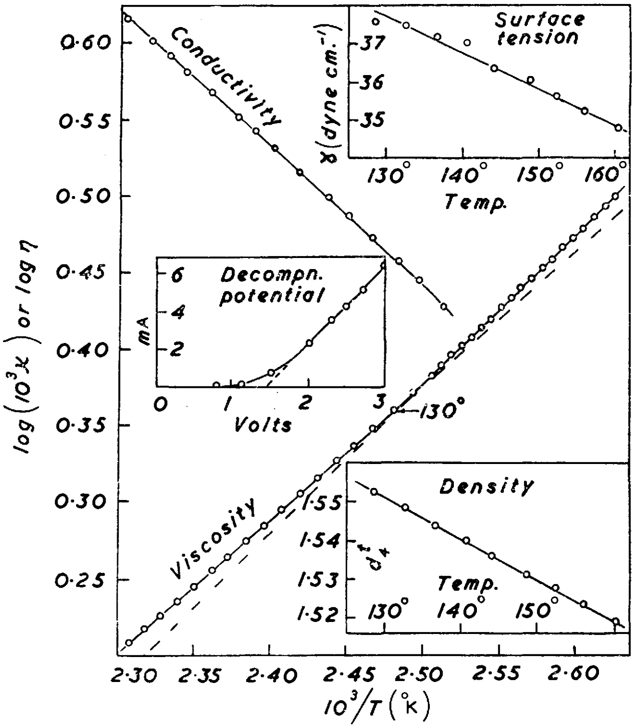

TABLE 1. *Electrical conductivity of* $GaCl_3,C_5H_5N$ *between* 125° *and* 160°.

No.	Temp.	$10^3\kappa$ (ohm^{-1} cm.$^{-1}$)	$\mu = \kappa V_M$ (cm.^{2} ohm^{-1} mole^{-1})	$\mu\eta$ (cm.^{2} cP ohm^{-1} mole^{-1})
8	124·8°	2·677	0·4387	1·076
9	127·5	2·784	0·4573	1·081
7	129·7	2·869	0·4719	1·082
10	132·3	2·968	0·4891	1·086
6	135·0	3·074	0·5075	1·089
11	137·2	3·157	0·5220	1·091
5	140·1	3·281	0·5436	1·098
12	143·0	3·394	0·5635	1·102
4	145·1°	3·479	0·5785	1·103
13	147·4	3·561	0·5929	1·103
3	150·2	3·697	0·6167	1·111
14	153·2	3·807	0·6365	1·107
2	155·2	3·906	0·6542	1·113
15	157·6	3·996	0·6702	1·114
1	160·4	4·134	0·6947	1·120

The 1 : 1 *complex* $GaCl_3,C_5H_5N$. Gallium trichloride–pyridine was prepared on the 30 g. scale and purified by repeated fractional freezing in vessels attached directly to the conductivity cell, viscometer, or dilatometer, and consisted of white crystals, m. p. (sharp) 126°.

The specific electrical conductivity, κ, which was reproducible and showed no variation over a period of 4 days, was measured in the temperature range 125—160°. Results, and the sequence of measurements, are in Table 1. At 126° the conductivity is $2{\cdot}725 \times 10^{-3}$ ohm^{-1} cm.$^{-1}$ and this corresponds to a molar conductivity, μ, of 0·4472 cm.^{2} ohm^{-1} mole^{-1} and a reduced conductivity, $\mu\eta$, of 1·077 cm.^{2} cP ohm^{-1} mole^{-1}, where η is the dynamic viscosity of the molten complex in cP. The approximate constancy of the reduced conductivity indicates that the molar conductivity is inversely proportional to the viscosity. As shown in Fig. 2, a plot of log κ against $1/T$ (°K) is very slightly curved, the mean slope corresponding to an activation energy for conduction, E_κ, of 4·16 kcal. mole^{-1}. The corresponding plot of log μ is also slightly curved and leads to a mean activation energy, E_μ, of 4·39 kcal. mole^{-1}.

A d.c. current–voltage experiment carried out on the complex between platinum electrodes at 133° indicated a decomposition potential of $1{\cdot}4_3$ v (Fig. 2). Above 1·1 v (0·28 mA) charring occurred at the anode; there was no visible reaction at the cathode. Because of this irreversible breakdown at the anode, back-e.m.f. values had little meaning since a reversible potential could not be established; after prolonged electrolysis the back-e.m.f. was about 0·3 v but this decreased rapidly with time.

The viscosity was measured in a sealed all-glass viscometer which employed the weir system to maintain a constant mean head of liquid at different temperatures. The kinematic viscosity, ν (centistoke), was computed from efflux times which varied between 60 and 110 sec. in the temperature range 108—160°. Dynamic viscosities, η (centipoise), were then obtained from the relation $\eta = \nu d$, where d is the density of the complex. The results, which showed no variation with time over a period of 36 hr., are in Table 2. At the m. p., 126°, the dynamic viscosity is $2{\cdot}40_8$ cP, *i.e.*, about twice the viscosity of water at room temperature. From the plot of log η against l/T (°K) (Fig. 2) it appears that there is a discontinous change in slope near the m. p. as the complex supercools; above 130° the activation energy of viscous flow, E_η, is 3·96 kcal. mole^{-1}, below this it is 4·47 kcal. mole^{-1}, an increase of 13%. These values are similar to those of E_κ and E_μ.

TABLE 2. *Viscosity of supercooled and molten* $GaCl_3,C_5H_5N$ *between* 108° *and* 160°.

Supercooled			Supercooled			Above m. p.			Above m. p.		
Temp.	ν (cs)	η (cP)	Temp.	ν (cs)	η (cP)	Temp.	ν (cs)	η (cP)	Temp.	ν (cs)	η (cP)
107·9°	2·006	3·158	116·9°	1·758	2·751	125·9°	1·551	2·412	144·2°	1·255	1·928
108·9	1·977	3·111	117·9	1·734	2·711	128·0	1·513	2·350	146·2	1·228	1·884
109·9	1·949	3·065	118·9	1·710	2·673	130·0	1·475	2·287	148·2	1·202	1·841
110·9	1·915	3·010	119·9	1·683	2·629	132·0	1·439	2·228	150·2	1·178	1·801
111·9	1·888	2·965	120·9	1·663	2·595	134·0	1·404	2·172	152·2	1·152	1·759
112·9	1·861	2·921	121·9	1·639	2·556	136·1	1·373	2·120	154·2	1·127	1·719
113·9	1·831	2·872	122·9	1·619	2·524	138·1	1·341	2·069	156·2	1·106	1·684
114·9	1·809	2·835	123·9	1·596	2·486	140·1	1·312	2·020	158·2	1·085	1·650
115·9	1·782	2·790	124·9	1·574	2·450	142·1	1·283	1·973	160·2	1·064	1·616

The density of a sample of the 1 : 1 complex which had been vacuum-distilled at temperatures well above the m. p. was virtually identical with that obtained on a sample purified by fractional refreezing, a fact which emphasizes the thermal stability of the compound:

$$\text{Distilled sample: } d_4^t = 1{\cdot}5563 - 1{\cdot}068 \times 10^{-3}(t - 125)$$

$$\text{Recrystallized sample: } d_4^t = 1{\cdot}5557 - 1{\cdot}070 \times 10^{-3}(t - 125)$$

Individual results from the first run, which extended from 125° to 160°, are shown graphically in Fig. 2.

The variation of surface tension in the same temperature range is given by

$$\gamma = 38{\cdot}2 - 0{\cdot}097(t - 125) \text{ dyne cm.}^{-1}$$

The corresponding equation for the molar surface free energy, ω, is

$$\omega = \gamma V_M{}^{2/3} = 1143 - 2{\cdot}34(t - 125) \text{ erg mole}^{-2/3}$$

In these equations V_M is the molar volume and the constant 2·34 is the Eötvös constant k. The parachor ($[P] = V_M\gamma^{1/4}$) is independent of temperature and has a mean value of 408·1 ($\pm$0·3 r.m.s.).

The vapour pressure of gallium trichloride–pyridine is $<10^{-1}$ mm. at the m. p. but rises to about 1 mm. at 175° and 10 mm. at 220°. The detailed results are given in Table 3 which also records the sequence of measurements as an indication of their reproducibility and the stability of the complex. The plot of log p against $1/T(°\text{K})$ is slightly curved but has an average slope corresponding to a heat of vaporisation of 20·3 kcal. mole^{-1}. The ratio $\Delta H_{\text{vap}}/E_\eta$ has the rather high value of 5·1. Another point of interest is that the vapour pressure curve extrapolates to a " boiling point " of about 350°; this may be compared with the approximate value obtained from the surface free-energy curve which extrapolates to a critical point ($\omega = 0$) of 615° and hence to a b. p. of about 320° if one uses the relation $(t_{\text{b.p.}} + 273) = (\frac{2}{3})(t_{\text{c.p.}} + 273)$. Neither extrapolation is expected to be particularly precise but both indicate similar values for the b. p.

TABLE 3. *Vapour pressure of* $GaCl_3,C_5H_5N$ *between* 150° *and* 250°.

No.	Temp.	p (mm. Hg)	No.	Temp.	p (mm. Hg)	No.	Temp.	p (mm. Hg)	No.	Temp.	p (mm. Hg)
1	153·9°	0·36	4	183·6°	1·91	6	209·4°	5·83	20	233·0°	15·33
2	167·0	0·69	8	188·2	2·31	12	215·8	8·21	16	235·5	15·60
3	170·4	0·77	5	194·2	3·15	13	220·0	9·23	19	240·5	19·25
9	176·6	1·12	7	199·6	4·02	14	224·5	10·92	18	245·3	21·98
10	178·4	1·39	11	204·6	4·86	15	230·0	13·05	17	250·4	24·44

These results on the 1 : 1 compound are discussed further below.

The 1 : 2 *complex* $GaCl_3,2C_5H_5N$. Gallium trichloride–dipyridine was prepared by the reaction of 7·435 g. of gallium trichloride with 6·682 g. of pyridine (mole ratio 1 : 2·0008). However, there was slight loss of pyridine during the subsequent manipulation of the complex and the m. p. was about 4° below the value of 113° obtained from the phase studies. This is unlikely to affect values of the other physical properties appreciably but the difficulties in handling this readily dissociating complex render the determination of its properties somewhat less accurate than those of the exceptionally stable 1 : 1 complex to which it tends to revert. In particular it was necessary to keep the gas space above the 1 : 2 complex as small as possible to minimize loss of pyridine from the liquid arising from the equilibrium

$$GaCl_3,2C_5H_5N \rightleftharpoons GaCl_3,C_5H_5N + C_5H_5N$$

The compound could frequently be cooled almost to room temperature before crystallization set in.

The electrical conductivity was measured in the range 103—136° and was reproducible to within 1 in 1000 at a given temperature during 5 hr. Recharging the cell with a different sample of complex also left the conductivity unchanged. Table 4 lists the results. For comparison with the 1 : 1 complex one can select values at 126°: the specific conductivity, κ, is 11·86 × 10^{-3} ohm^{-1} cm.$^{-1}$, the molar conductivity, μ, is 2·95 cm.^{2} ohm^{-1} mole^{-1}, and the reduced conductivity, $\mu\eta$, is 5·82 cm.^{2} cP ohm^{-1} mole^{-1}. These figures show that the 1 : 2 complex conducts some 4—7 times better than the 1 : 1 complex, depending on the particular measure of conduction used (and the temperature).

TABLE 4. *Electrical conductivity of molten and supercooled* $GaCl_3,2C_5H_5N$ *between* 103° *and* 136°.

No.	Temp.	$10^3\kappa$ (ohm^{-1} cm.$^{-1}$)	$\mu = \kappa V_M$ (cm.^{2} ohm^{-1} mole^{-1})	$\mu\eta$ (cm.^{2} cP ohm^{-1} mole^{-1})	No.	Temp.	$10^3\kappa$ (ohm^{-1} cm.$^{-1}$)	$\mu = \kappa V_M$ (cm.^{2} ohm^{-1} mole^{-1})	$\mu\eta$ (cm.^{2} cP ohm^{-1} mole^{-1})
5	103·2°	7·78	1·88	7·95	21	117·9°	10·54	2·59	6·46
7	103·6	7·85	1·90	7·90	12	119·6	10·83	2·67	6·31
8	105·6	8·23	1·99	7·65	20	122·1	11·23	2·77	6·11
6	106·8	8·46	2·05	7·51	13	123·8	11·49	2·85	5·99
4	107·1	8·61	2·09	7·56	19	126·7	11·98	2·98	5·77
9	108·7	8·86	2·15	7·32	14	128·0	12·12	3·02	5·66
3	110·3	9·16	2·23	7·14	18	130·3	12·47	3·11	5·49
10	112·3	9·54	2·33	6·95	15	132·2	12·70	3·18	5·38
2	114·3	9·90	2·42	6·74	17	133·8	12·91	3·24	5·28
11	115·8	10·20	2·50	6·63	16	135·7	13·11	3·29	5·14
1	117·9	10·53	2·59	6·45					

The plot of log κ against $1/T$ (°K) is a smooth curve, the activation energy E_κ decreasing steadily from 6·86 kcal. mole^{-1} at the lower temperatures to 3·30 kcal. mole^{-1} at high temperatures. Similarly E_μ decreases from 7·64 to 3·59 kcal. mole^{-1}. At 126° E_κ = 3·96 and E_μ = 4·21 kcal. mole^{-1}, values which are very close to those for the 1 : 1 complex (4·16 and 4·39 respectively).

The viscosity of gallium trichloride–dipyridine is given in Table 5. It was reproducible over a period of days and is similar to that of the 1 : 1 complex, the two quantities being identical at the m. p. of the 1 : 2 complex, 113°. However, the viscosity of the 1 : 2 complex changes more rapidly with temperature, E_η varying from 11·05 kcal. mole^{-1} at low temperatures to 7·78 kcal. mole^{-1} at high temperatures. At 126° E_η = 7·80 kcal. mole^{-1} (4·47 kcal. mole^{-1} for the 1 : 1 complex). The activation energy for viscous flow of the 1 : 2 complex is greater than for any other complex of gallium trichloride yet investigated though it is approached by the 1 : 2 complex with piperidine discussed in the following paper. Because the activation energy for conduction is not also abnormally large it follows that conductivity and viscosity are not strictly inversely proportional and $\mu\eta$ falls as the temperature rises (Table 4). This point will be amplified in the Discussion.

TABLE 5. *Viscosity of molten and supercooled* $GaCl_3,2C_5H_5N$ *between* 103° *and* 137°.

Temp.	ν (cs)	η (cP)	Temp.	ν (cs)	η (cP)	Temp.	ν (cs)	η (cP)	Temp.	ν (cs)	η (cP)
103·0°	3·077	4·262	113·0°	2·128	2·911	123·0°	1·589	2·148	133·0°	1·244	1·661
105·0	2·845	3·929	115·0	1·990	2·716	125·0	1·502	2·025	135·0	1·191	1·586
107·0	2·636	3·634	117·0	1·878	2·558	127·0	1·429	1·922	137·0	1·138	1·512
109·0	2·444	3·360	119·0	1·774	2·409	129·0	1·361	1·826			
111·0	2·275	3·119	121·0	1·672	2·265	131·0	1·295	1·734			

The density run was not as extensive as the others but the following equation was derived from results obtained between 92° and 107°:

$$d_4^t = 1{\cdot}389 - 1{\cdot}64 \times 10^{-3}(t - 100)$$

In the temperature range 92—102° the surface tension was about 50 dyne cm.$^{-1}$ and the parachor 640 but it is probable that these values are quite inaccurate owing to the depletion in pyridine of the surface layers of complex as a result of thermal dissociation, and little reliance is placed on them.

DISCUSSION

The most striking effect of complex formation in the system gallium trichloride–pyridine is the great increase in electrical conductivity. The published values for the specific conductivities of molten gallium trichloride [6] and pyridine [10] are 2×10^{-6} and 4×10^{-8} ohm^{-1} cm.$^{-1}$ respectively, whereas for the complexes near their m. p.s the values are 3×10^{-3} and 1×10^{-2}. It is therefore important to enquire what ions are present and to what extent the complexes are dissociated into kinetically free ions. In the absence of direct evidence probable structures for the complexes can be inferred by a process of elimination.

The simple formula (I) for the 1 : 1 complex is unsatisfactory since it leaves unexplained the high electrical conductivity and does not account for the ability of the complex to take up a further mole of pyridine, unless a pentaco-ordinate complex of gallium is postulated for the 1 : 2 compound. The similarity in m. p., conductivity, viscosity, and other physical properties of the two complexes suggests that their structures are similar. Ionization by separation of a chloride ion (II) is unlikely as it leaves the gallium atom electron-deficient in the presence of a strong electron donor, Cl^- (cf. Ga_2Cl_6). The cation $[C_5H_5N{\rightarrow}GaCl_2]^+$ in structure (II) could, however, be stabilized by the addition of a further molecule of pyridine to give $[(C_5H_5N)_2GaCl_2]^+Cl^-$, the structure suggested for the 1 : 2 complex (below). Structure (III) for the 1 : 1 complex involves ionization of an α-hydrogen atom from the pyridine molecule and is untenable for a variety of reasons. First, no gas

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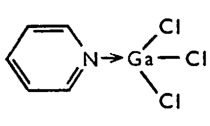
[10] Walden, Audrieth, and Birr, *Z. phys. Chem.*, 1932, **160**, *A*, 337.

is evolved during electrolysis of the molten complex, suggesting that hydrogen ions are absent. This evidence becomes more cogent when coupled with the analogous behaviour of the corresponding piperidine complex discussed in the following paper, for with piperidine there is no possibility that cathodic reduction of the ligand could remove the nascent hydrogen. Secondly, there is no apparent means of solvating the bare proton unless it be with a second undissociated molecule of complex as shown in structure (I); even



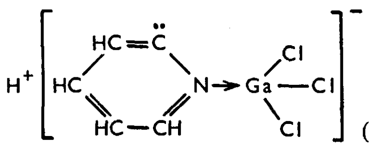
(I)

$[C_5H_5N\rightarrow GaCl_2]^+Cl^-$

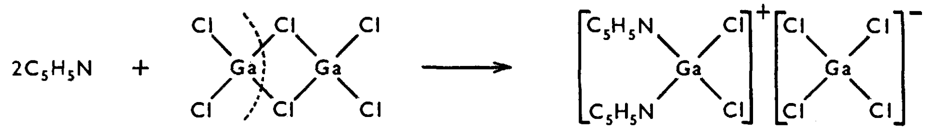
(II)

$[C_5H_5NH]^+[C_5H_4N\rightarrow GaCl_3]^-$

(IV)



(III)



(V)

then, the only non-bonding electrons available for donation to the proton are those on the chlorine atoms. The situation is thus rather different from that which obtains, for example, with oxygen-containing complexes of boron trifluoride [11] since the oxygen atom, unlike nitrogen, has a second lone pair of electrons available to solvate the proton. Finally, a 1 : 1 complex of hypothetical structure (III), which is essentially an anhydrous acid, would be far less stable than the corresponding 1 : 2 complex (IV) which is its pyridinium salt. The reverse is true, the 1 : 1 complex being the more stable. Reference to the complexes of boron trifluoride is again relevant for, in those systems which are known to furnish hydrogen ions, the 1 : 2 complexes are invariably the more stable.[11] For these reasons, structures (I)—(IV) cannot be accepted.

A structure (V) which accounts for the observed facts can be derived from the gallium trichloride dimer. The molten complex should be an ionic conductor, but hydrogen would not be evolved on electrolysis. Moreover, structure (V) explains the great similarity in properties of this complex and gallium trichloride–phosphorus oxychloride, $POCl_2^+GaCl_4^-$ (m. p. 118·5°, $\kappa = 1{\cdot}26 \times 10^{-3}$, $\mu = 0{\cdot}227$, $\mu\eta = 0{\cdot}442$, $E_\kappa = 4{\cdot}10$, $\eta = 1{\cdot}95$, $E_\eta = 3{\cdot}41$, $\Delta H_{vap} = 18$, etc.).[7] The presence of a large cation in both these complexes lowers the m. p. below that of other tetrachlorogallates such as $Ga^+GaCl_4^-$, m. p. 170°, and $K^+GaCl_4^-$, m. p. 259°.

An instructive analogy can also be drawn between the 1 : 1 complex $GaCl_3,C_5H_5N$ (m. p. 126°) and the corresponding complexes BCl_3,C_5H_5N (m. p. 115°) [12] and $AlCl_3,C_5H_5N$ (m. p. 118°).[13] Infrared data on the boron complex have been interpreted in terms of the structure $[py_2BCl_2]^+BCl_4^-$,[12] and an analogous formula $[py_2AlCl_2]^+AlCl_4^-$ would explain the observation [13] that the aluminium complex is dimeric in benzene but monomeric in nitrobenzene; clearly the ionic formulation suggested here would lead to an apparent molecular weight equal to that of monomeric $AlCl_3,C_5H_5N$ if ionic dissociation were complete, as it may well be in nitrobenzene (dielectric constant $\varepsilon = 35{\cdot}7$), whereas in a solvent of very low dielectric constant such as benzene ($\varepsilon = 2{\cdot}3$) association into ion pairs would lead to a molecular weight corresponding to the dimer $(AlCl_3,C_5H_5N)_2$.

The 1 : 2 complex between gallium trichloride and pyridine is most simply considered as the chloride corresponding to structure (V): $[py_2GaCl_2]^+Cl^-$. Thus, no hydrogen

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[11] Greenwood and Martin, *Quart. Rev.*, 1954, **8**, 1.

[12] Greenwood, Wade, and Perkins, 16th Congress I.U.P.A.C. (Inorganic Section), Paris 1957, in the press.

[13] Eley and Watts, *J.*, 1952, 1914.

would be expected on electrolysis as would be the case with structure (IV) and the lower stability of the complex could be related to the disparity in size of the cation and anion. An alternative structure for the 1 : 2 complex which cannot be eliminated on the present evidence is $[py_4GaCl_2]^+GaCl_4^-$, though this is perhaps less likely in view of the normal preference of gallium for tetrahedral rather than octahedral co-ordination. It is hoped to obtain more definite evidence on the nature of the ions present in these complexes by Raman spectroscopy and nuclear magnetic resonance. Thus, although the Raman spectrum of the cation $[py_2GaCl_2]^+$ is expected to be complicated, it may be possible to identify the four lines characteristic of $GaCl_4^-$ in the molten 1 : 1 complex. Similarly, if structure (V) is correct there are two chemically different types of gallium atom in the complex and these might be detected by studying the chemical shifts in the high-resolution nuclear magnetic resonance spectrum of gallium in the molten complex. By contrast, the suggested structure for the 1 : 2 complex does not contain the $GaCl_4^-$ ion and all the gallium atoms are in the same chemical environment.

The extent to which the 1 : 1 and 1 : 2 complexes are ionically dissociated into kinetically free units requires some discussion. From arguments previously outlined[14] the degree of ionic dissociation (α, %) should be given approximately by the expression

$$\alpha = 100\ M\kappa\eta/(2d\boldsymbol{N}\boldsymbol{e}v_0) = 50\ \mu\eta/(\boldsymbol{N}\boldsymbol{e}v_0)$$

In these expressions M is the monomeric molecular weight, κ the specific conductivity, η the dynamic viscosity (cP), d the density and v_0 an assumed average mobility of the ions in a medium having a viscosity of 1 cP. For moderately-sized ions, such a mobility is normally about 5×10^{-4} cm.^{2} sec.$^{-1}$ v^{-1} and if this and the numerical values of $\boldsymbol{N}$ and $\boldsymbol{e}$ are substituted then the quantity $50/(\boldsymbol{N}\boldsymbol{e}v_0)$ becomes (fortuitously) equal to unity, so that the percentage degree of dissociation is given directly by the reduced conductivity $\mu\eta$. In the case of the 1 : 1 compound $[py_2GaCl_2]^+GaCl_4^-$ it would be more appropriate to use the dimeric molecular weight for M so that $\alpha = 2\mu\eta$. On this basis, the complex would appear to be dissociated to the extent of about 2% into kinetically free ions, the corresponding figure for the 1 : 2 complex being about 5—8%.

Two observations should be made: (i) The calculated degree of ionic dissociation for the 1 : 1 complex is of the same order as that calculated for $POCl_2^+GaCl_4^-$.[7] On the other hand, the Raman spectrum of the molten phosphorus oxychloride complex can be interpreted in terms of complete (100%) ionization into $POCl_2^+GaCl_4^-$.[15] The distinction is between ionization and ionic dissociation and the difference in the two values may be due to ion-pair formation which would not influence the number of lines in the Raman spectrum but would reduce the number of kinetically free ions. A value of 2% for the ionic dissociation should therefore not be taken as necessarily implying that the remaining 98% of the complex is molecular; it may well be ionic as in the case of the phosphorus oxychloride complex. (ii) The calculation of the degree of ionic dissociation assumes that the ionic mobility is viscosity-controlled so that conductivity is exactly inversely proportional to viscosity. This is not the case for the 1 : 2 complex and, instead of E_η being equal to E_μ, the ratio E_η/E_μ is approximately 1·4, which is larger than that for any other complex studied. As a result, the value of $\mu\eta$ decreases with rise in temperature. This could be interpreted as arising from a change in the number of kinetically free ions with temperature (decrease in α) but it is not considered that the method of calculation is sufficiently refined to interpret this change in terms of equilibrium constants, free energies, and entropies of ionic dissociation as has recently been suggested.[16] An alternative and more plausible interpretation is that the mechanisms of conduction and viscosity, though similar, are not identical so that the ionic mobility is not entirely viscosity-controlled.

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[14] Greenwood and Martin, *J.*, 1953, 1427.

[15] Woodward (Chem. Soc. Meeting at Cambridge, 1957), *Chem. Soc. Special. Publ.* No. 8, in the press.

[16] Bradley, *Trans. Faraday Soc.*, 1956, **52**, 1255.

The postulated ions for the 1 : 2 complex, $[py_2GaCl_2]^+$ and Cl^-, are very different in size. In such a situation, conduction may occur relatively easily by migration of the smaller ions through the interstices in the disordered network of the larger ions, whereas viscous flow involves the configurational breakdown or shear of the larger ions over each other. The activation energy of conduction would then be less than that of viscous flow, as observed for the 1 : 2 complex. A similar situation is well known for the alkali-metal halides where E_η remains approximately constant for a given halogen whilst E_μ, which is considerably smaller than E_η, increases from the lithium halide to the cæsium halide as the size of the cation increases.[17]

THE UNIVERSITY, NOTTINGHAM.

[*Received, November* 18*th*, 1957.]

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[17] Bloom and Heymann, *Proc. Roy. Soc.*, 1947, *A*, **188**, 392.