331. *Addition Compounds of Gallium Trichloride. Part VI.*[1] *Complexes with Piperidine.*

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The new addition compounds $GaCl_3,C_5H_{10}NH$ (m. p. 134°) and $GaCl_3,2C_5H_{10}NH$ (m. p. 112°) have been studied to determine what effect the removal of the aromatic character from pyridine has on the electron-donor properties of the ligand. The two piperidine complexes are very similar to the corresponding pyridine complexes though certain differences in detail appear, which can be ascribed to the buckling of the heterocyclic ring when saturated. The complexes are ionic and can be formulated as $[pip_2GaCl_2]^+GaCl_4^-$ and $[pip_2GaCl_2]^+Cl^-$.

Piperidine differs from pyridine in at least three ways which might be expected to influence its properties as a ligand: (*a*) the absence of aromatic character, (*b*) the buckling of the ring, and (*c*) the presence of an *N*-hydrogen atom. The removal of aromatic character increases the electron density near the nitrogen atom and so increases the donor strength of the ligand; for example, piperidine forms a 1 : 1 addition compound with trimethyl borate $(MeO)_3B$ whereas pyridine does not,[2] and the heat of addition of piperidine to stronger electron acceptors such as boron trichloride or gallium trichloride is greater than that of pyridine.[3] However, in the case of a strong electron acceptor, moderate variations in the actual strength of the donor–acceptor bond may not alter the physical properties of the complexes appreciably provided that the temperature at which comparison is made is not so great as to dissociate the bond.

Ring buckling increases the steric requirements of the piperidine molecule and this may influence the stability of a complex if there are a considerable number of such ligands surrounding a very small acceptor atom. Where this is not so, the most likely effect of substituting piperidine for pyridine would be to increase those properties (such as molar volume and Batschinski's constant) which depend to some extent on molecular dimensions, and to influence those properties which depend, at least in part, on molecular symmetry (such as activation energy of viscous flow). These considerations clearly apply equally to the ligands themselves and it will be shown that the molar volume, Batschinski constant, and activation energy of viscous flow are all greater for piperidine than for pyridine.

The third difference between the two ligands is the presence of an *N*-hydrogen atom in piperidine. It is unlikely that hydrogen bonding would occur in the piperidine complexes since there is no evidence that it plays a significant part in modifying the properties of the

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[1] Part V, Greenwood and Wade, preceding paper.

[2] Venkataramaraj, Urs, and Gould, *J. Amer. Chem. Soc.*, 1952, **74**, 2948.

[3] Greenwood, Wade, and Perkins, 16*th Congress I.U.P.A.C.* (*Inorganic Section*), Paris 1957, in the press; Greenwood, Proc. Symposium on Coordination Chemistry, Rome, 1957, in the press.

ligands themselves; for example, the b. p. and dynamic viscosity of piperidine are both less than, not greater than, those of pyridine. On the other hand, the mode of ionization of piperidine complexes might well be determined by the relative ease or difficulty of ionizing the N–H bond. Changes in the distribution of electronic charge following co-ordination involving the non-bonding electrons on the nitrogen atom should facilitate ionization of the proton, but energetically still more favourable ways of ionizing it might conceivably exist.

This work was undertaken to answer questions arising from speculations of this type. The 1 : 1 and the 1 : 2 complex of piperidine resemble the corresponding pyridine complexes very closely in many properties; this is ascribed to a similarity in their ionic structure. The absence of cathodic hydrogen on electrolysis eliminates the possibility of ionization's involving hydrogen ions and the complexes are best considered in terms of complex cations containing tetrahedrally co-ordinated gallium: $[pip_2GaCl_2]^+GaCl_4^-$ and $[pip_2GaCl_2]^+Cl^-$. On the basis of these structures a detailed interpretation of the similarities and differences between the complexes and those of pyridine is possible.

EXPERIMENTAL AND RESULTS

Preparation, purification, and methods were as in the preceding paper.[1] Piperidine (m. p. $-4°$, b. p. 106·3°) was dried (KOH or BaO) before being fractionated.

When successive amounts of piperidine were condensed on gallium trichloride in a vacuum line, the m. p. of the system varied as shown in Fig. 1, which also incorporates results obtained in the region 50—80 moles % of piperidine by evaporating this component out of the reaction vessel after the first set of readings had been taken. The two sets of results substantially agree, which implies that only piperidine is volatile over mixtures containing more piperidine than would correspond to the 1 : 1 complex. There were maxima at 50 moles % ($GaCl_3,C_5H_{10}NH$, m. p. 134°) and 66·7% ($GaCl_3,2C_5H_{10}NH$, m. p. 112°). The eutectics could not be obtained satisfactorily because of extensive supercooling but graphically they can be placed at about 28 moles % of piperidine ($<0°$), at 59% ($\sim 100°$), and at about 90% ($<-5°$). As in the pyridine system, the flatter maximum of the 1 : 2 compound indicates that it was more dissociated in the liquid phase than was the 1 : 1 compound. In agreement with this, whereas the vapour pressure of the 1 : 1 complex was negligible below 160°, the 1 : 2 complex had a vapour pressure of about 13 mm. Hg at room temperature (cf. 20—25 mm. for piperidine itself).

The 1 : 1 *Complex*, $GaCl_3,C_5H_{10}NH$.—The specific electrical conductivity was measured at 1000 cycles/sec. on a specimen purified as usual by successive fractional freezings under vacuum in an apparatus sealed directly to the conductivity cell. A conductivity–temperature run between the m. p. (134°) and 174° showed that the complex decomposed slowly above 150°; for example, the specific conductivity increased by 2% during 2 hr. at 151° and by 10% in 3 hr. at 170°. A second run on this now slightly modified sample gave results which were quite reproducible between 128° and 143° but were about 14% higher than those for the compound when originally sealed in the cell. The results of this second run are given in Table 1 which indicates the sequence of measurements; the duration of the run was 12 hr. At the m. p. the specific conductivity, κ, is $1·969 \times 10^{-3}$ ohm^{-1} cm.$^{-1}$, the molar conductivity, μ, is 0·346 cm.^{2} ohm^{-1} mole^{-1}, and the reduced conductivity, $\mu\eta$, is 1·63 cm.^{2} cP ohm^{-1} mole^{-1}. The specific conductivity of the sample when first melted was $1·70 \times 10^{-3}$ ohm^{-1} cm.$^{-1}$ at the m. p.

The figures in Table 1 lead to a temperature coefficient which is probably quite accurate, since it agrees with the coefficient calculated from the few reliable low-temperature readings obtained on the first run. The plots of log μ (Fig. 2) and log κ against $1/T°$(K) are linear throughout the range; $E_\kappa = 5·61$ kcal. mole^{-1}, $E_\mu = 5·87$ kcal. mole^{-1}.

D.C. current–voltage curves at 139° indicated a decomposition potential of 0·58 v for the molten 1 : 1 complex and this low value was confirmed in a back-e.m.f. experiment in which the maximum value was 0·5 v. No gas was evolved during electrolysis between bright platinum electrodes but a charred deposit was observed streaming down from the anode. After 15 minutes' electrolysis at 2—4 mA the anode was covered with a black deposit and the cathode had turned dull. The A.C. resistance of the cell was virtually unchanged after the D.C. experiment.

The viscosity of a carefully purified sample of gallium trichloride–piperidine was measured in a sealed, weir-type viscometer between 122° and 160°. Measurements, taken on four successive days (Table 2), indicate both the reproducibility of the measurements and the stability of the complex insofar as it affects the viscosity. Efflux times varied between 100 and 200 sec. and correspond, at the m. p., to a dynamic viscosity of $4{\cdot}71_3$ cP. The plot of log η against $1/T$(°K) given in Fig. 2 is probably better fitted by a smooth curve rather than by two straight lines, although there seems to be a region of maximum curvature at about 137°. The activation energy E_η decreases from 6·28 kcal. mole^{-1} at low temperatures to 5·84 kcal. mole^{-1}

FIG. 1. *Phase diagram of the system* $GaCl_3$–$C_5H_{10}NH$.

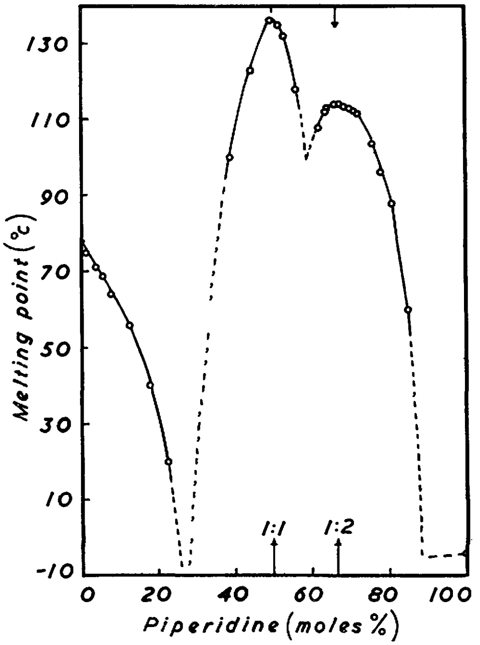

FIG. 2. *Properties of molten* $GaCl_3,C_5H_{10}NH$.

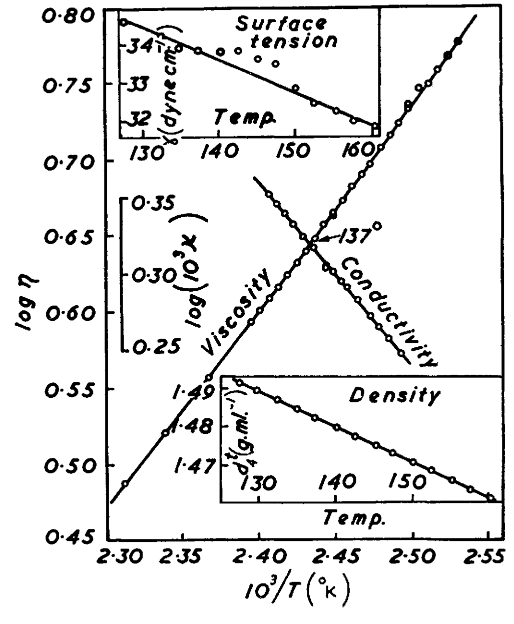

TABLE 1. *Electrical conductivity of* $GaCl_3,C_5H_{10}NH$ *between* 128° *and* 143°.

No.	Temp.	$10^3\kappa$ (ohm^{-1} cm.$^{-1}$)	μ (cm.^{2} ohm^{-1} mole^{-1})	$\mu\eta$ (cm.^{2} cP ohm^{-1} mole^{-1})
4	128·0°	1·770	0·3099	1·640
5	129·3	1·810	0·3174	1·639
6	130·2	1·841	0·3228	1·638
7	131·2	1·872	0·3285	1·627
2	132·5	1·916	0·3365	1·632
8	133·7	1·954	0·3435	1·629
3	134·1	1·974	0·3470	1·632
9	135·1	2·002	0·3522	1·629
1	136·1°	2·037	0·3586	1·622
17	136·1	2·043	0·3596	1·627
10	137·2	2·075	0·3656	1·619
11	138·3	2·112	0·3722	1·619
12	139·3	2·148	0·3789	1·619
13	140·3	2·185	0·3857	1·619
14	141·2	2·217	0·3914	1·617
15	142·1	2·251	0·3978	1·617
16	143·2	2·292	0·4052	1·617

TABLE 2. *Viscosity of* $GaCl_3,C_5H_{10}NH$ *between* 122° *and* 159°.

Supercooled			Molten			Supercooled			Molten		
Temp.	ν (cS)	η (cP)	Temp.	ν (cS)	η (cP)	Temp.	ν (cS)	η (cP)	Temp.	ν (cS)	η (cP)
121·9°	3·997	5·984	129·0°	3·483	5·192	135·0°	3·104	4·608	142·1°	2·749	4·065
122·9	3·911	5·851	130·0	3·423	5·099	136·1	3·060	4·540	143·2	2·701	3·990
123·9	3·827	5·722	131·0	3·339	4·970	137·1	2·994	4·439	144·2	2·656	3·920
124·9	3·762	5·622	132·1	3·291	4·896	138·1	2·947	4·366	149·2	2·454	3·611
125·9	3·689	5·508	133·0	3·231	4·803	139·1	2·894	4·286	154·2	2·268	3·327
126·9	3·612	5·389	134·0	3·172	4·713	140·1	2·847	4·213	159·2	2·108	3·081
127·9	3·547	5·290				141·1	2·797	4·136			

at the higher temperatures. The activation energy for viscous flow of the complex above its m. p. is therefore almost identical with the activation energy for molar conduction (E_μ = 5·87 kcal. mole^{-1}), so that the product $\mu\eta$ remains virtually constant above this temperature.

The density and surface tension between 127° and 161° are also plotted in Fig. 2. The density can be represented (±0·0001) by

$$d_4^t = 1{\cdot}4847 - 9{\cdot}38 \times 10^{-4}(t - 135) \text{ g. ml.}^{-1}$$

The surface tension results show some scatter but can be represented to within ±1·5% by

$$\gamma = 34{\cdot}05 - 8{\cdot}47 \times 10^{-2}(t - 135) \text{ dyne cm.}^{-1}$$

The corresponding equation for the surface free energy is

$$\omega = \gamma V_M^{\frac{2}{3}} = 1069 - 2{\cdot}34(t - 135) \text{ erg mole}^{-\frac{2}{3}}$$

in which V_M is the molar volume and 2·34 is the Eötvös constant k. The equation can be extrapolated to zero surface free energy (critical temperature) at 592° whence a very approximate value of the "boiling point" of the complex can be obtained as $\{\frac{2}{3}(592 + 273) - 273\}$, *i.e.*, 305°. This is some 70° below an equally approximate value estimated by extrapolating the vapour-pressure measurements from 13 mm. to 760 mm.

The parachor ($[P] = V_M\gamma^{\frac{1}{4}}$) of the 1 : 1 complex is constant in the temperature range studied and is 425·2 ± 0·8 (r.m.s.), a value remarkably close to the value of 424·4 obtained by McGowan's method [4] for the hypothetical structure $C_5H_{11}N{\rightarrow}GaCl_3$. The agreement is probably fortuitous since the proposed structure of the complex, $[pip_2GaCl_2]^+GaCl_4^-$, although it has the same number of covalent bonds, is essentially that of a molten salt for which parachor calculations are notoriously unreliable. Thus, the observed and calculated parachors for the corresponding pyridine complex differ by 20·1 units. The main use of the parachor in such circumstances is not as a guide to molecular structure, but as a check, by its constancy, on the reliability of the surface-tension measurements.

Vapour-pressure experiments in which the 1 : 1 complex was heated to 245° appeared to result in slight decomposition with the formation of residual gas, there being a final pressure of 3·0 mm. in the apparatus at room temperature after a typical run. Results obtained during 5 hr. on a freshly recrystallized sample of complex, which had been degassed under vacuum by short immersion in a bath at 170°, are listed in Table 3. They correspond to the equation

$$\log p \text{ (mm.)} = 9{\cdot}811 - 4486/T$$

which leads to a latent heat of evaporation, ΔH_{vap}, of 20·5$_3$ kcal. mole^{-1}. The ratio $\Delta H_{\text{vap}}/E_\eta$ has the reasonable value 3·52.

TABLE 3. *Vapour pressure of molten* $GaCl_3,C_5H_{10}NH$ *between* 159° *and* 242°.

Temp.	159·3°	176·0°	184·2°	193·8°	202·4°	211·1°	220·0°	232·0°	242·1°
p (mm. Hg)	(0·01)	0·51	1·01	1·63	2·42	3·51	5·23	8·26	12·84

The 1 : 2 *Complex* $GaCl_3,2C_5H_{10}NH$.—The complex (m. p. 112°) was synthesized to within 1 part in 10^4 (w/w) by condensing 6·0497 g. of freshly fractionated piperidine on 6·2556 g. of gallium trichloride in a vacuum line. Because of the high vapour pressure of piperidine above the complex the compound could not be purified by fractional crystallization but care was taken in all manipulations to transfer the complex quantitatively *in vacuo*. Thus, the conductivity cell was fitted with a receiving limb into which the compound was sealed after the measurements had been made and this was in turn sealed into the viscometer unit (which in this instance did not incorporate a glass sinter for vacuum filtration because of the risk of losing piperidine from the melt). The volumes were such that even if the pressure above the 1 : 2 complex reached 1 atm. the change in composition of the liquid phase would be less than 1 mole % of piperidine in the conductivity experiments and about 3 moles % in the viscosity measurements.

The conductivity of molten gallium trichloride–dipiperidine between 105° and 138° is listed

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[4] McGowan, *Rec. Trav. chim.*, 1956, **75**, 193.

in Table 4 and plotted logarithmically in Fig. 3. There was no pronounced drift at any temperature but the check-reading at 123·9° showed that the conductivity had increased by 0·38% during 2½ hr. This slight decomposition was confirmed on a second sample which gave readings some 3% higher than those obtained on the first run after having been deliberately heated for about 1 hr. at 145°. However, such variations should in no way invalidate the main conclusions to be drawn from the investigation (see Discussion). For comparison with the 1 : 1 compound, the value of the specific conductivity, κ, at 134° can be calculated to be $1{\cdot}279 \times 10^{-3}$ ohm^{-1} cm.$^{-1}$ which corresponds to a molar conductivity, μ, of 0·340 cm.^{2} ohm^{-1} mole^{-1} and a reduced conductivity, $\mu\eta$, of 1·37 cm.^{2} cP ohm^{-1} mole^{-1}. At this temperature, therefore, the conductivities of the two complexes are very similar, those of the 1 : 2 complex being slightly the smaller. This difference is emphasized if comparison is made at the respective melting points, but even then the reduced conductivities of the two complexes remain similar.

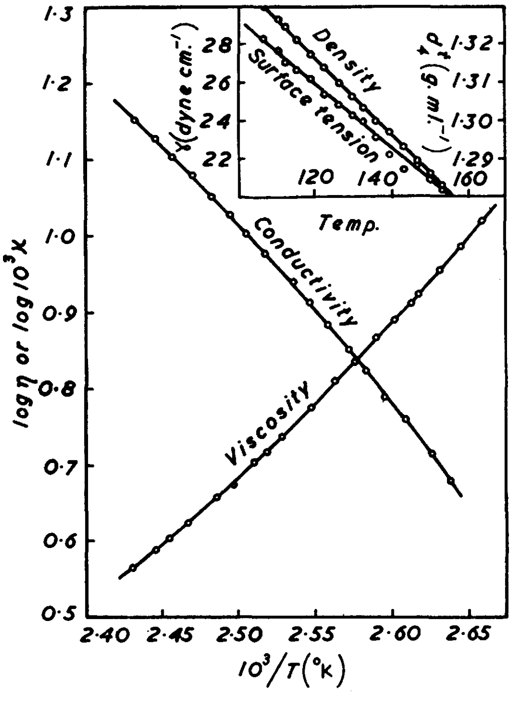

FIG. 3. *Properties of molten* $GaCl_3,2C_5H_{10}NH$.

The activation energy of conduction, E_κ, varied from 11·79 kcal. mole^{-1} at lower temperatures to 9·12 kcal. mole^{-1} at the higher temperatures. Corresponding values for E_η are 11·90 and 9·70 kcal. mole^{-1} respectively. These high values, which are paralleled by high values for E_η, are nearly twice as great as the figures obtained for the 1 : 1 complex. A similar effect

TABLE 4. *Electrical conductivity of* $GaCl_3,2C_5H_{10}NH$ *between* 106° *and* 138°.

No.	Temp.	$10^3\kappa$ (ohm^{-1} cm.$^{-1}$)	μ (cm.^{2} ohm^{-1} mole^{-1})	$\mu\eta$ (cm.^{2} cP ohm^{-1} mole^{-1})
17	105·8°	0·4789	0·1246	1·169
16	107·7	0·5205	0·1356	1·185
15	110·1	0·5750	0·1501	1·211
14	111·9	0·6172	0·1613	1·225
13	113·9	0·6663	0·1744	1·239
12	115·6	0·7117	0·1865	1·251
11	117·6	0·7674	0·2015	1·277
10	119·4	0·8189	0·2152	1·282
9	121·6	0·8810	0·2320	1·291
8	123·9°	0·9485	0·2504	1·301
18 *	123·9	0·9521	0·2511	1·304
7	125·8	1·008	0·2663	1·321
6	127·7	1·069	0·2828	1·333
5	129·7	1·127	0·2986	1·336
4	131·7	1·202	0·3193	1·363
3	133·8	1·272	0·3380	1·369
2	135·7	1·341	0·3572	1·382
1	137·8	1·419	0·3784	1·398

* After 5 hr. at various temperatures.

was noted for the viscosity of the two pyridine complexes of gallium trichloride, though in these the difference in activation energies of conduction was not so great.

The results of a viscosity run on the 1 : 2 complex between 102° and 138° are presented in Table 5 and Fig. 3. Readings were taken on three successive days. At 134° (the m. p. of the 1 : 1 compound) the dynamic viscosity, η, is 4·03 cP which is similar to the viscosity of the 1 : 1 complex. The activation energy, however, is greater, as just mentioned, and varies considerably with temperature, decreasing from 10·08 to 7·65 kcal. mole^{-1} in the temperature range investigated. It is not easy to ascribe this variation predominantly to changes in composition of the melt due to loss of piperidine since the viscosity of the 1 : 1 complex is so similar to that of the 1 : 2 complex.

TABLE 5. *Viscosity of* $GaCl_3,2C_5H_{10}NH$ *between* 102° *and* 138°.

Temp.	ν (cS)	η (cP)	Temp.	ν (cS)	η (cP)	Temp.	ν (cS)	η (cP)	Temp.	ν (cS)	η (cP)
102·9°	7·839	10·463	111·1°	5·865	7·779	122·2°	4·154	5·461	132·2°	3·234	4·220
104·9	7·264	9·680	112·9	5·559	7·362	123·7	3·980	5·227	134·1	3·083	4·016
106·9	6·773	9·012	114·9	5·170	6·837	125·1	3·852	5·053	135·6	2·981	3·878
108·9	6·340	8·422	116·9	4·901	6·471	127·3	3·596	4·710	138·1	2·827	3·670
109·6	6·170	8·193	119·3	4·535	5·977	129·1	3·468	4·535			

The density and surface tension of gallium trichloride–dipiperidine between 105° and 155° are also shown in Fig. 3. The density can be expressed to within 0·05% by the equation

$$d_4^t = 1{\cdot}3253 - 1{\cdot}026 \times 10^{-3}(t - 112) \text{ g. ml.}^{-1}$$

Similar equations which reproduce the surface tension to within 0·2 dyne cm.$^{-1}$ and the molar surface free energy to within 20 erg mole$^{-2/3}$ are

$$\gamma = 27{\cdot}3 - 0{\cdot}167(t - 112) \text{ dyne cm.}^{-1}; \ \omega = 1123 - 6{\cdot}56\ (t - 112) \text{ erg mole}^{-2/3}$$

As with the 1 : 2 pyridine complex, these surface properties are sensitive to slight changes in composition at the interface and this may explain the anomalously large temperature coefficient of surface tension and Eötvös constant (6·56 erg deg.$^{-1}$ mole$^{-2/3}$). This explanation is also consistent with the parachor values which, unlike those of the nonvolatile 1 : 1 complexes which were constant, decreased from 600 to 575 as the temperature rose from 105° to 155°. It is not profitable to modify this trend by using the full parachor formula $[P] = \gamma^{1/4}M/(d_{liq} - d_{gas})$ since the composition of the gas phase is not the same as that of the liquid. Moreover, simple application of the extended formula, made on the assumption that the vapour above the liquid phase is, in fact, the 1 : 2 complex, shows that an increase in vapour pressure of the order of 2 atm. would be required to account for the observed drop in parachor over the temperature range of 50°. Change in composition of the surface is thus the more probable explanation.

DISCUSSION

From a comparison of corresponding properties it is at once apparent that the complexes of gallium trichloride with pyridine and piperidine are closely similar, any differences being of detail rather than of kind. The arguments of the preceding paper, applied to the present compounds, lead to the formulæ $[pip_2GaCl_2]^+GaCl_4^-$ and $[pip_2GaCl_2]^+Cl^-$ and are based on the following main lines of evidence: (i) The 1 : 1 complex can add a further mol. of ligand to give the 1 : 2 complex; (ii) both complexes are good electrical conductors when molten (Table 6); (iii) the properties of the 1 : 2 complex are similar to those of the 1 : 1 complex except that it dissociates more readily; and (iv) electrolysis does not result in cathodic evolution of hydrogen. Similarly, the extent to which the compounds are dissociated into kinetically free ions can be estimated if the standard ionic mobility used for the pyridine complexes[1] is adopted for the piperidine complexes also. The degree of dissociation (α) of the 1 : 1 complexes is then given by $2\mu\eta$ and is about 2% for $GaCl_3$,py and about 3% for $GaCl_3$,pip; the value for the 1 : 2 complexes is given by $\mu\eta$ directly and is about 6% for $GaCl_3$,2py and about 1% for $GaCl_3$,2pip. These estimates should be correct to within a factor of 2 or 3.[5] Reference to Table 6 shows that the values of α for the complexes are far greater than those for gallium trichloride and the ligands themselves which are virtually un-ionized. It is also noteworthy that the degree of ionic dissociation of the complexes is practically independent of both the ligand and the combining ratio and varies little with temperature. The values can not yet be discussed in more detail because of the approximate nature of the calculations and the uncertain interpretation of the calculated degrees of dissociation not being nearer 100%. Two further topics, however, arise from Table 6: (*a*) the viscosity of the complexes, their activation energies, and Batschinski constants; and (*b*) the similarity in m. p. of the complexes.

TABLE 6. *Comparison of some conduction and viscosity characteristics.*

Compound	M. p.	$10^3\kappa_{120}$	$(\mu\eta)_{120}$	η_{120}	E_μ	E_η	10^2B
Ga_2Cl_6	77·8°	0·002	$3·6 \times 10^{-4}$	1·038	(~1)	3·64	5·75
Pyridine	—41·8	<0·001	$\sim10^{-5}$	0·339	—	2·67	6·43
Piperidine............	—10·5	<0·001	$\sim10^{-4}$	0·283	—	3·82	8·50
$GaCl_3$,py	126	2·50	1·07	2·626	4·39	3·96	7·63
$GaCl_3$,2py	113	10·89	6·28	2·332	4·21	7·80	7·03
$GaCl_3$,pip	134	1·50	1·65	6·240	5·87	5·84	10·6
$GaCl_3$,2pip	112	0·836	1·28	5·852	11·9	10·1	14·6

The dynamic viscosities of the complexes of gallium trichloride with pyridine and piperidine are all greater than the viscosities of their components. For example, the results in Table 6 show that, at the arbitrarily chosen temperature of 120°, the viscosity of the pyridine complexes is about 7 times greater than that of pyridine itself; the factor for the piperidine complexes is about 21. Moreover, the viscosity of the 1 : 2 complexes is less than that of the corresponding 1 : 1 compounds; in this the complexes resemble those of boron trifluoride for which also the viscosity of the 1 : 1 complex is always the greater.[6]

The activation energy, E_η, is also increased by co-ordination in agreement with the ionic nature of the complexes. Thus, in general, activation energies of viscous flow for molecular liquids (including non-polar, polar, hydroxylated, and hydrogen-bonded liquids) are small and fall in the range 0·4—4 kcal. mole^{-1} whereas those for highly ionized molten salts (such as the alkali halides) fall mainly in the range 4—10 kcal. mole^{-1}.[7] Table 6 indicates that the present donors, acceptor, and complexes conform to this classification. It is also seen that the activation energies for piperidine and its complexes are larger than those of pyridine and its complexes respectively; this seems reasonable in view of the piperidine molecule's being far less symmetrical than the planar pyridine molecule owing to the buckling effect of its tetrahedral carbon bond angles. It may also be significant that the 1 : 2 complexes have higher activation energies than those of the 1 : 1 complexes. At first sight this may seem surprising, as the 1 : 2 complexes contain a greater proportion of the ligands (L) which have low activation energies. However, activation energies should be roughly inversely proportional to the sum of the ionic radii since the larger the ions the more nearly do they approach a molecular, non-ionic configuration and the smaller the influence of the unit charges. The effect is therefore understandable in terms of the suggested structures, as the 1 : 1 complexes involve two moderately large ions, $[L_2GaCl_2]^+GaCl_4^-$, whereas the 1 : 2 complexes involve only one, $[L_2GaCl_2]^+Cl^-$.

Values of Batschinski's constant B (ml. cP g.$^{-1}$)are tabulated in the last column of Table 6. The constant, which is a rough guide to the size of the flow units in a liquid, can be obtained from the relation $\eta = B/(v - b)$ in which v is the specific volume and b a

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

[6] *Idem, Quart. Rev.*, 1954, **8**, 1.

[7] Ward, *Trans. Faraday Soc.*, 1937, **33**, 88.

constant. The equation implies a linear relation between specific volume and fluidity, $v = b + B\phi$, and this holds to a fair degree of approximation for the 1 : 1 complexes above their m. p.s. Deviations from linearity are more marked for the 1 : 2 complexes, the slope decreasing with rise in temperature. The values listed in Table 6 can be interpreted as follows: (*a*) the value for piperidine is greater than that for pyridine because of the greater steric requirements of the buckled ring. The values for the piperidine complexes are greater than those for the pyridine complexes for the same reason; (*b*) complex formation increases the value of B. Thus, the values for the pyridine complexes are greater than those for either pyridine or gallium trichloride alone and the same is true for the piperidine complexes. This is consistent with the presence of large ions such as $[L_2GaCl_2]^+$ but does not prove their existence since an increase would also be expected for simple molecular addition compounds of the type $L\rightarrow GaCl_3$; (*c*) the Batschinski constant for the 1 : 2 pyridine complex is *smaller* than that for the 1 : 1 complex. The same is true for certain complexes of boron trifluoride (*e.g.*, the hydrates [8]) and in each case the values are consistent with the relative sizes of the postulated ions. For example, both pyridine complexes contain the same cation, $[py_2GaCl_2]^+$, but the anion of the 1 : 2 complex, Cl^- is *smaller* than that of the 1 : 1 complex, $GaCl_4^-$. Similarly both hydrates contain the same anion, $[BF_3{\cdot}OH]^-$, but the cation of the 1 : 2 complex, H_3O^+, is *smaller* than that of the 1 : 1 complex, $[H_3O{\cdot}BF_3]^+$. The piperidine complexes do not conform to these considerations, the value of B for the 1 : 2 complex being larger than that for the 1 : 1 complex despite the fact that the postulated anion is smaller. Such reversals in the relative values of Batschinski's constant are not unknown [9] and emphasize the care which must be taken in drawing detailed conclusions about molecular structure from the bulk properties of compounds.

The similarity in m. p. observed for the four complexes of gallium trichloride with pyridine and piperidine is not confined to these complexes alone but is part of a curious and hitherto unexplained tendency shown by a variety of complexes between electron-deficient halides and various ligands.[10] This is illustrated in Table 7: the m. p.s of the 19 complexes all fall within a range of 14° whereas the m. p.s of the constituent donor and acceptor moieties are spread evenly over a range of 326°. Many other examples could be chosen and, although exceptions such as the complex BCl_3,pip which melts at 184° are also known, yet it remains true that an extraordinary number of complexes melt between 100° and 150°. This is hard to understand if the complexes are considered as covalent molecules (because of the wide variation in molecular weight) but is quite consistent with their formulation as ionic compounds. The fact that their m. p.s are lower than those of many molten salts is ascribed to the presence of large ions, the greater interionic distances reducing the Coulomb attractive force and hence lowering the m. p. It is significant that the m. p.s of many substituted ammonium picrates fall within the same range, *e.g.*, Pr^n_3NHPic, m. p. 114°, Pr^n_4NPic, m. p. 119°, and n-$C_7H_{15}NH_3Pic$, m. p. 124°. These compounds by their nature must be ionic and, moreover, they have similar conduction characteristics to those of the present complexes.[5]

If the explanation advanced in the preceding paragraph to account for the similarities in the m. p.s of complexes is correct, then it follows that all the complexes listed in Table 7 are ionic. The aluminium halide complexes with ammonia and pyridine have previously been considered as molecular [10] despite the fact that, in those cases where the electrical conductivity of the molten complexes has been studied,[11] the molar conductivities were very similar to those of the complexes of gallium trichloride investigated here. The confusion appears to have arisen because the estimated degree of ionic dissociation of the

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[8] Greenwood, *J. Inorg. Nuclear Chem.*, 1958, **5**, 224, 229.

[9] Greenwood and Worrall, *ibid.*, in the press.

[10] Klemm and Tanke, *Z. anorg. Chem.*, 1931, **200**, 343; Klemm, Tilk, and Jacobi, *ibid.*, 1932, **207**, 187; Eley and Watts, *J.*, 1952, 1914.

[11] Klemm, Clausen, and Jacobi, *Z. anorg. Chem.*, 1931, **200**, 367.

ammines was of the order of 1%; the rest of the structure was considered to comprise covalent molecules rather than ion pairs as in the present interpretation. Again, the Raman spectrum of the molten complex $AlCl_3,NH_3$, which consists of 20 lines, has been interpreted in terms of an " ethane-like " molecular structure $H_3N,AlCl_3$.[12] This structure would be expected to give 12 lines, as observed for example in the isoelectronic compound methyltrichlorosilane, $H_3C{\cdot}SiCl_3$. The discrepancy was qualitatively ascribed to an assumed distortion of the structure which reduced the symmetry and hence increased the number of lines. As against this, the ionic structure now suggested, *viz.*, $[(NH_3)_2AlCl_2]^+AlCl_4^-$, should give a spectrum of 20 lines, as observed, since it can be considered as the sum of two spectra similar to those of the isoelectronic species $(CH_3)_2SiCl_2$ (16 lines) and $SiCl_4$ (4 lines). Whilst it is realized that mere enumeration of lines without a detailed study of their position, intensity, and polarization affords no proof of the structure, it does suggest that the reported assignments for this compound might profitably be reinvestigated.

TABLE 7. *Melting points of some complexes and their parent compounds.*

M. p. 112—115°	M. p. 117—120°	M. p. 124—126°	Ligands		Acceptors	
BCl_3,py	$AlCl_3$,py	$AlCl_3,NH_3$	NH_3	− 78°	BCl_3	−107°
$AlBr_3$,dioxan	$AlBr_3$,py	$AlBr_3,NH_3$	py	− 42°	$AlCl_3$	193°
AlI_3,py	$AlBr_3,PH_3$	AlI_3,NH_3	pip	− 11°	$AlBr_3$	97°
$GaCl_5$,2py	AlI_3,PH_3	$GaCl_3,NH_3$	PH_3	−133°	AlI_3	191°
$GaCl_3$,2pip	$GaCl_3,POCl_3$	$GaBr_3,NH_3$	Dioxan	12°	$GaCl_3$	78°
$GaBr_3,POCl_3$ *	$GaCl_3,Ph_3CCl$ *	$GaCl_3$,py	$POCl_3$	1°	$GaBr_3$	122°
		$GaBr_3$,py *	Ph_3CCl	112°		

* Unpublished observations in this laboratory.

There is no suggestion that all complexes of the Group III halides and related compounds have structures similar to those now proposed. Other structures are well known;[6] for example, the complexes of boron trifluoride with ammonia and pyridine have been shown by *X*-ray analysis to have the structures H_3N,BF_3[13] and py,BF_3.[14] However, these compounds have widely differing m. p.s and stabilities [H_3N,BF_3, m. p. 163° (decomp.)[15]; py,BF_3, m. p. 48°[6], b. p. 300°[16]] and appear to differ also from the compounds listed in Table 7 in their electrochemical properties, where these have been investigated. For example, boron trifluoride–pyridine, which is ionically dissociated to a small extent when molten, evolves hydrogen at the cathode on electrolysis whereas boron trichloride–pyridine does not. Such differences will be discussed more fully later.

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[12] Goubeau and Siebert, *Z. anorg. Chem.*, 1947, **254**, 126.

[13] Hoard, Geller, and Cashin, *Acta Cryst.*, 1951, **4**, 396; Hoard, Geller, and Owen, *ibid.*, p. 405.

[14] Zvonkova, *Kristallografiya*, 1956, **1**, 73.

[15] Laubengayer and Condike, *J. Amer. Chem. Soc.*, 1948, **70**, 2274.

[16] van der Meulen and Heller, *ibid.*, 1932, **54**, 4404.