Aqueous solutions of trivalent gallium salts with added NH$_4$F or HF have been investigated using $^{19}$F and $^{69,71}$Ga NMR. Four species have been identified in the solutions: GaF$_2$·aq$^+$, GaF$_3$·aq$^-$, GaF$_4$·aq, and GaF$_6$·aq$^+$. The relative equilibrium constants for the formation of these complexes have been determined. In the presence of competing ligands (F$^-$, H$_2$O), distortion of the octahedral configuration or a change in the coordination number of the gallium is possible.

Aluminum (III), gallium (III), and indium (III) form a series of complexes with different compositions with fluoride ions. The successive formation constants for all the possible species from AlF$_2^+$ to AlF$_6^+$ have been determined for the fluoroaluminates [1]. In the case of indium, the formation constants for InF$_2^+$, InF$_3^+$, InF$_4^-$ and InF$_5^-$ are known [2], while for gallium only the formation constant for GaF$_2^+$ has been found experimentally [3, 4]. For GaF$_2^+$, GaF$_3^+$, GaF$_4^-$, and GaF$_5^2^-$, the calculated dissociation constants are $1.6 \times 10^{-1}$, $1.8 \times 10^{-3}$, $3 \times 10^{-1}$ and 0.5, respectively [5].

The formation constants for the monofluorocomplexes in accordance with the reaction

$$M \cdot \text{aq}^{3+} + F \cdot \text{aq}^- \rightleftharpoons MF \cdot \text{aq}^{2+}$$

are $(1.23 \pm 0.11) \times 10^6$, $(2.38 \pm 0.21) \times 10^4$, and $(5.3 \pm 0.4) \times 10^3$ for Al$^{3+}$, Ga$^{3+}$, and In$^{3+}$, respectively [4], which indicates that the monofluorocomplexes become less stable as one passes from the top to the bottom of a subgroup.

Connie and Poulson [6] confirmed the existence of AlF$_2^+$ and AlF$_3^+$ in solution by means of $^{19}$F NMR and, in later papers [7, 8], the number of species shown to exist in solution increased to four: AlF·aq$^+$, AlF$_2$·aq$^+$, AlF$_3$·aq, and AlF$_4$·aq$^+$. No signals corresponding to individual species were discovered in the spectra of Ga(CIO$_4$)$_3$·AgF solutions. Two signals were observed. One of these was assigned to F$^-$ and the broad signal at higher fields arose as the result of the formation of the various different complexes GaF$_n$·3F$^-$ [9] in solution.

In the present paper an attempt has been made to use the $^{19}$F NMR method in order to identify the complex species present in fluoride solutions of gallium, to estimate the formation constants for these species, and to study ligand substitution in the first coordination sphere of the fluorogallates.

The method used to record the $^{19}$F NMR spectra was the same as that used in previous works [10]. Gallium chloride, prepared by chlorination of the metal*, was used as the initial reagent. The gallium content in the solutions was determined by a gravimetric method after precipitation with ammonia solution. The total acidity was determined by titration with a solution of KOH. The solutions which were used to record the spectra were prepared by weighing solutions of GaCl$_3$ with additions of known amounts of a 32% solution of NH$_4$F or 48% solution of HF into polyethylene tubes.

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Fig. 1. The $^{19}$F NMR spectra of GaCl$_3$ - NH$_4$F.

Spectra typical of solutions containing gallium (III) and fluoride ion are shown in Fig. 1. At the lowest $F:Ga$ ratio investigated, there are two signals in the spectra. The chemical shifts for these two signals are rather close together at about 2.5 ppm apart. These signals can only be assigned to different fluorogallate complexes since, as the concentration of fluoride ion in the solution is increased, the relative intensity of these signals changes and a new signal appears at lower field which increases in intensity as more ammonium fluoride is added to the solution. This corresponds to the build up in the solution of a species containing a larger amount of fluoride in the first coordination sphere of gallium. By allowing for the dependence of the spectral contour on the $F:Ga$ ratio, we have assigned the signal in the 580 ppm region to the monofluorocomplex of gallium. Species containing two or three fluoride atoms give $^{19}$F NMR signals at lower fields than GaF$_2^{aq+}$. A similar dependence was also observed in fluoroaluminate solutions [8]. As in the case of aluminum, the range of chemical shifts observed in a solution of fluorogallates is not very large (less than 5 ppm).

The concentration formation constants for the fluorocomplexes of gallium can be estimated from the data on the relative integral intensities. These formation constants are defined by the equations

$$
K_1 \frac{[GaF^{aq+}][GaF\cdot aq^{+}]}{[Ga\cdot aq^{3+}][GaF\cdot aq^{+}]};
$$
$$
K_2 \frac{[GaF\cdot aq^{+}][GaF_2\cdot aq^+]}{[Ga\cdot aq^{3+}][GaF\cdot aq^{+}]};
$$
$$
K_3 \frac{[GaF\cdot aq^{+}][GaF_2\cdot aq^+]}{[GaF^aq^{2+}][GaF\cdot aq^{+}]};
$$
$$
K_4 \frac{[GaF^aq^{2+}][GaF\cdot aq^{+}]}{[GaF\cdot aq^{+}][GaF_2\cdot aq^+]};
$$
$$
K_5 \frac{[GaF\cdot aq^{+}][GaF_2\cdot aq^+]}{[GaF\cdot aq^{+}][GaF\cdot aq]}.
$$

We did not succeed in observing a signal from the $F\cdot aq^+$ ion from any of the solutions. Apparently, its concentration in solution is lower than the sensitivity of the instrument. Hence, we only had the data for the calculation of the relative constants at our disposal. These relative constants are

$$
K_1 = \frac{[GaF^{aq+}][GaF\cdot aq^{+}]}{[Ga\cdot aq^{3+}][GaF\cdot aq^{+}]};
$$
$$
K_2 = \frac{[GaF\cdot aq^{+}][GaF_2\cdot aq^+]}{[Ga\cdot aq^{3+}][GaF\cdot aq^{+}]};
$$
$$
K_3 = \frac{[GaF\cdot aq^{+}][GaF_2\cdot aq^+]}{[GaF^aq^{2+}][GaF\cdot aq^{+}]};
$$
$$
K_4 = \frac{[GaF\cdot aq^{+}][GaF_2\cdot aq^+]}{[GaF\cdot aq^{+}][GaF\cdot aq]};
$$
$$
K_5 = \frac{[GaF\cdot aq^{+}][GaF_2\cdot aq^+]}{[GaF\cdot aq^{+}][GaF\cdot aq]}.
$$

For the concentrations of gallium chloride which were investigated (from 0.73 to 1.52 mole/1000 g of solution), the ratios of the constants were $K_1/K_2 = 2.52$ (the mean of 16 determinations), $K_2/K_3 = 4.40$ (the mean of 15 determinations), $K_3/K_4 = 3.68$ (the mean of 4 determinations). It was not possible to make use of the known formation constant of GaF $aq^{2+}$ [4] in the calculation since, in the cited paper, the measurements were carried out in solutions with an ionic strength corresponding to 1 N NaClO$_4$ while, in the solutions investigated by us, the ionic strength varied from 6 to 8.

As distinct from the GaCl$_3$ - NH$_4$F solutions, a signal from free HF in the presence of GaF $aq^{2+}$, GaF$_2$ $aq^+$ and GaF$_3$ $aq$ showed up in the spectra of GaCl$_3$ - HF solutions at $F:Ga$ molar ratios of greater than 1.5. The simultaneous existence of fluorogallates and HF in solution at sufficiently low $F:Ga$ ratios indicates that the dissociation constants for HF and GaF$_3$ $aq$ must be quantities of the same order of magnitude.

As far as the possibility of other ligands entering into the primary coordination sphere of the identified fluorogallates is concerned, this may be judged from indirect data. For example, in aqueous GaCl$_3$ - NH$_4$F, Ga(CIO$_4$)$_3$ - NH$_4$F, and Ga$_2$(SO$_4$)$_3$ - NH$_4$F solutions, the chemical shifts of the signals arising from the fluorocomplexes are practically identical. It might therefore be proposed that, in perchloric solutions, there are water molecules in the primary coordination sphere of the gallium ions in addition to fluoride ions. On passing to the chloride or sulfate ion,