301. *Raman Spectrum and Constitution of Fused Gallium Dibromide.*

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Gallium dibromide was prepared as a white crystalline compound, m. p. 166·7°. Its Raman spectrum in the fused state at approx. 180° was in close agreement with that previously found for the $GaBr_4^-$ ion in aqueous solution. In the fused state, therefore, gallium dibromide is to be formulated as $Ga^+[GaBr_4]^-$. This conclusion is supported by the electrical conductivity of the melt, and is also consistent with the observed diamagnetism of the solid.

The structure of gallium dibromide is of interest since the empirical formula $GaBr_2$ appears to indicate a valency of 2 for gallium, whereas the normal valency of Group III elements is 3 or 1. Very little is to be found in the literature about the compound. The original preparation of gallium dibromide has been attributed [1] to Lecoq de Boisbaudran; but although in 1878 he briefly announced the preparation of several anhydrous halides of gallium [2] and subsequently distinguished the dichloride [3] from the trichloride, his publications do not appear to contain any reference to the dibromide. The first evidence for the existence of a lower bromide seems to have been given in 1930 by Johnson and Parsons,[4] who reported a relatively involatile residue in their tribromide preparation. The promised paper describing the properties of the lower bromide has never appeared. The dibromide was mentioned in 1932 by Klemm and Tilk,[5] but again the promised further report has not appeared. In 1934 Miescher and Wehrli [6] described briefly the preparation of a compound, stated to be the dibromide, by a method analogous to that used for the dichloride, *i.e.*, by reduction of the tribromide with excess of gallium metal. As far as we are aware, no subsequent publication on the compound has appeared; but we are informed by Mr. F. M. Brewer that it has been prepared in Oxford a number of times by his collaborators,[7] who have studied some of its properties and in particular shown it to have the empirical formula $GaBr_2$.

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[1] Gmelin-Kraut, " Handbuch der anorganischen Chemie," Winter, Heidelberg, 1911, Vol. 4, 1, p. 214; Mellor, " Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1925, Vol. 5, p. 384.

[2] Lecoq de Boisbaudran and Jungfleisch, *Compt. rend.*, 1878, **86**, 577; Lecoq de Boisbaudran, *ibid.*, p. 756.

[3] Lecoq de Boisbaudran, *ibid.*, 1881, **93**, 294.

[4] Johnson and Parsons, *J. Phys. Chem.*, 1930, **34**, 1210.

[5] Klemm and Tilk, *Z. anorg. Chem.*, 1932, **207**, 161.

[6] Miescher and Wehrli, *Helv. Phys. Acta*, 1934, **7**, 331.

[7] Spencer-Palmer, Chemistry Part II Thesis, Oxford, 1941; Garton, D.Phil. Thesis, Oxford, 1953.

No investigation of the structure of gallium dibromide has been reported. If the molecular formula were $GaBr_2$, the compound would be paramagnetic. Analogy with the dichloride suggests, however, that it will have the formula Ga_2Br_4 and be diamagnetic. As with the dichloride, the question then arises as to whether the structure is of the covalent type $Br_2Ga–GaBr_2$, involving a bond between two gallium atoms, or of the ionic type $Ga^+[GaBr_4]^-$, in which the apparent valency of 2 is due to the univalency of one of the gallium atoms and the tervalency of the other.

A recent study of the Raman spectrum of fused gallium dichloride[8] has decided in favour of the ionic structure for that compound. The present paper reports similar work for the dibromide.

Results and Discussion.—The Raman spectrum of gallium dibromide in the fused state at approx. 180° (*i.e.*, approx. 13° above its m. p.) consisted of four frequencies and is described in Table 1, which gives observed frequency shifts together with estimated intensities, appearances, and states of polarisation of the lines. For comparison, Table 2 reproduces the spectrum obtained by Woodward and Nord[9] for the tetrabromogallate ion, $GaBr_4^-$, in an aqueous solution of gallium tribromide containing excess of hydrobromic acid. The number of lines and their states of polarisation prove that the ion is a regular tetrahedron (point-group T_d). The appropriate assignments are included in Table 2. The very close similarity of the two spectra is obvious, and the case is thus analogous to that of the fused dichloride.[8] Within the estimated limits of error of the measured $\Delta\nu$ values, the frequency ν_1 of the most intense, strongly polarised line is practically identical in Tables 1 and 2. Each of the two lower frequencies of the dibromide also agrees closely with the corresponding frequency of the tetrabromogallate ion. The highest frequency appears in both spectra as a diffuse Raman line (breadth approx. 35 cm.$^{-1}$) whose centre (as given in Tables 1 and 2) is difficult to locate precisely; but here also the difference between the two spectra is not large.

TABLE 1. *Raman spectrum of fused gallium dibromide.*

$\Delta\nu$ (cm.$^{-1}$)	79	107	209	288
Intensity	Strong	Strong	Very strong	Weak
Appearance	Sharp	Sharp	Sharp	Diffuse
Polarisation	Depolarised	Depolarised	Strongly polarised	Depolarised

TABLE 2. *Raman spectrum of the* $GaBr_4^-$ *ion in aqueous solution.*

$\Delta\nu$ (cm.$^{-1}$)	71	102	210	278
Intensity	Strong	Strong	Very strong	Rather weak
Appearance	Sharp	Sharp	Sharp	Diffuse
Polarisation	Depolarised	Depolarised	Strongly polarised	Depolarised
Assignment	$\nu_2\ (E)$	$\nu_4(F_2)$	$\nu_1(A_1)$	$\nu_3(F_2)$

These findings prove that fused gallium dibromide contains $GaBr_4^-$ ions as the predominant polyatomic species. The close agreement between the spectra is remarkable in view of the considerable difference to be expected between the interactions in molten gallium dibromide on the one hand and aqueous solution at room temperature on the other. We conclude that the vibrational frequencies of the tetrabromogallate ion (like those of the tetrachlorogallate ion[8]) are insensitive to environmental changes. As discussed at greater length for fused gallium dichloride,[8] the observed spectrum is not consistent with the presence of $Br_2Ga–GaBr_2$ molecules or any ionic species derivable therefrom by the dissociation of bromide ions. Therefore, the melt is to be formulated as gallium(I) tetrabromogallate(III), $Ga^+[GaBr_4]^-$.

This conclusion is supported by other measurements. First, experiment showed that

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[8] Woodward, Garton, and Roberts, *J.*, 1956, 3723.

[9] Woodward and Nord, *J.*, 1955, 2655.

(like the dichloride[10]) the solid dibromide at room temperature is diamagnetic, which rules out the molecular formula $GaBr_2$. Secondly, the electrical conductivity of the melt is close to that of many fused salts, especially those in which the cation is considerably smaller than the anion. Table 3 gives the values of the specific conductivity κ, the molar conductivity μ, and the reduced conductivity $\mu\eta$ (where η is the dynamic viscosity) for fused gallium dibromide at its m. p. 166·7°. For comparison, Table 3 includes corresponding data[11] for fused silver nitrate at about 11° above its m. p. The values of the specific conductivity for the two compounds are of the same order of magnitude; the molar conductivities are more nearly equal; and when allowance for viscosity is made, the reduced conductivities are practically identical. That the melt is ionic is thus supported by the electrical conductivity.

TABLE 3. *Electrical conductivity of fused gallium dibromide.*

	Temp.	κ (ohm^{-1} cm.$^{-1}$)	μ (ohm^{-1} cm.^{2} mole^{-1})	$\mu\eta$ (ohm^{-1} cm.^{2} mole^{-1} cP.)
Fused $Ga^+GaBr_4^-$	166·7°	0·1491	19·73	136·4
Fused $Ag^+NO_3^-$	220	0·693	29·8	135

EXPERIMENTAL

Preparation and Purification of Gallium Dibromide.—Gallium tribromide[12] was heated at 180° in a sealed evacuated tube with slightly less than the theoretical weight of gallium metal. When all the gallium had dissolved, most of the excess of tribromide was sublimed from the mixture by cooling one end of the reaction tube in a blast of air. During this sublimation, which required several days, the m. p. of the mixture rose from 150° to 158°. Further purification was by fractional crystallisation of the melt, one-fifth of the sample being discarded in each cycle. The first crystallisation raised the m. p. to 164°, and after five more cycles it had become constant at 166·7°. The solid was colourless.

It is not feasible to prepare pure gallium dibromide by heating the tribromide with excess of gallium metal[6] and subliming the product in a vacuum, for the dibromide slowly disproportionates above 200°.

Determination of Physical Properties.—The dibromide was repurified before each experiment by fractional freezing in a vessel attached directly to the measuring apparatus (conductivity cell, viscometer, etc.) which was finally sealed off without breaking the vacuum.[13]

Raman Spectrum.—The apparatus (Toronto arc excitation, Hilger E 518 spectropraph) has been described.[14] The purified gallium dibromide was transferred to the Raman vessel *in vacuo*. During the exposures it was kept molten at approx. 180° by a stream of electrically preheated air passing through the annular space between the Raman vessel and the surrounding Dewar sleeve. The molten sample was clear and pale straw-yellow. It was nevertheless possible to observe the Raman spectrum excited by the blue mercury line 4358 Å and the violet line 4046 Å. Indeed, the scattering was found to be intense. By using Kodak special scientific plates (type Oa, sensitivity G) the complete Raman spectrum from the blue line 4358 Å could be photographed with an exposure time of only 5 min. Longer times revealed no new features. A slight continuum appeared in the region between Hg 4358 Å and Hg 4916 Å, which might have tended to mask weak Raman lines with the longer exposures. However, this continuum (presumably due to a trace of fluorescence) was almost completely suppressed by using as filter an aqueous solution of sodium nitrite or, better, a benzene solution of *m*-dinitrobenzene. There was no sign of deterioration of the sample as a result of the repeated melting and irradiation.

Qualitative determinations of the states of polarisation of the Raman lines were made by the method of polarised incident light, oriented polaroid cylinders surrounding the Raman tube. Frequencies were measured in the usual manner with a copper-arc spectrum as standard. The

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[10] Klemm and Tilk, *Z. anorg. Chem.*, 1932, **207**, 175.

[11] Landolt and Börnstein, "Physikalisch-chemische Tabellen," 5th edn., Berlin, 1923. More recent determinations are in substantial agreement.

[12] Greenwood and Worrall, *J. Inorg. Nucl. Chem.*, 1957, **3**, 357.

[13] Greenwood and Wade, *J.*, 1957, 1516; *J. Inorg. Nucl. Chem.*, 1957, **3**, 349.

[14] Rolfe and Woodward, *Trans. Faraday Soc.*, 1954, **50**, 1030; Woodward and Roberts, *J.*, 1956, 1170.

estimated limits of error of the $\Delta\nu$ values are about ± 2 cm.$^{-1}$ for the strong sharp lines. The value given in Table 1 for the highest frequency, which appeared as a diffuse line, refers to the estimated centre and may be subject to a larger error.

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