Vibrational Spectra and Metal–Metal Bonding in the Hexahalogenodigallate(II) Ions, $Ga_2X_6^{2-}$ (X = Cl, Br, and I)

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The title ions have been prepared as tetra-alkylammonium salts and their i.r. and Raman spectra are reported and assigned according to D_{3d} symmetry. Normal-co-ordinate calculations have been made for $Ga_2Cl_6^{2-}$ which indicate a Ga–Ga force constant of 217 N m^{-1}.

HEXAHALOGENODIGALLATE(II) ions are present in the strongly reducing solutions of gallium metal in halogen acids [1,2] and have been isolated as crystalline Me_4N^+ salts.[2] The suggested ethane-like structure, with a gallium–gallium bond, has since been confirmed by a single crystal X-ray analysis of $(Me_4N)_2Ga_2Cl_6$.[3] These novel gallium(II) ions take part in the anodic oxidation of the metal in HCl or HBr electrolytes [2,4] and in lower halide formation by the elements.[5,6] Here we describe the preparation and complete vibrational spectra of $Ga_2Cl_6^{2-}$, $Ga_2Br_6^{2-}$, and $Ga_2I_6^{2-}$ as tetra-alkylammonium salts.

In using these spectra for structural diagnosis a particularly striking feature is the intense Raman band in the region *ca.* 100—250 cm^{-1} associated with 'metal-metal stretching' vibrations.[7-9] For $Ga_2Cl_6^{2-}$ this band is shown by normal co-ordinate analysis to arise from a mixed mode involving in-phase metal-metal and metal-ligand stretching.

EXPERIMENTAL

Preparations.—The compounds $(R_4N)_2Ga_2X_6$ (R = Me, Et, or Pr^n; X = Cl or Br) were prepared from gallium metal (B.D.H. 99·9%) by anodic oxidation in 6M-HCl or HBr, respectively, followed by precipitation as the R_4N^+ salt. The metal was cast around Pt wire and this gallium electrode was made the anode of a cell with the halogen acid (ice-cold) as the electrolyte and a Pt coil as cathode. Electrolysis for 1 h at 80 mA current, followed by addition of an excess of a saturated solution of R_4NX in the appropriate acid precipitated a white solid. The solid was collected, washed with ethanol, dried *in vacuo*, and recrystallised from nitromethane to give colourless crystals. The gallium(II) compounds, $(R_4N)_2Ga_2X_6$, were obtained free from the gallium(III) compounds, R_4NGaX_4, as judged by i.r. spectra, and gave satisfactory elemental analyses. (Yield *ca.* 60% from the metal.)

The compounds $(Bu^n_4N)_2Ga_2X_6$ (X = Cl or Br) were prepared as mixtures with $Bu^n_4NGaX_4$ which could not be separated by recrystallisation.

Gallium(III) contamination of the initial precipitates, greater for electrolyses at room temperature, or with increased [HX], or time of electrolysis, was ascribed to oxidation of the Ga^{II} complex by hydrogen ions, as shown by effervescence of the electrolyte. However attempts to avoid oxidation by using lower HX concentrations led to deposition of gallium on the cathode, and to reduced yields of the gallium(II) compounds.

The $Ga_2I_6^{2-}$ ion was difficult to obtain in a pure compound. Anodic oxidation in HI electrolytes gave solutions of GaI_4^- only, as judged by their Raman spectra and the far i.r. spectra of the precipitated R_4N^+ salts. In an alternative method (which could also be used to prepare the $Ga_2Cl_6^{2-}$ or $Ga_2Br_6^{2-}$ salts), finely powdered gallium metal was dissolved in concentrated HI. Precipitation with saturated Me_4NI solution gave a mixture in which GaI_4^- was identified by vibrational spectra and the additional bands were attributed to $Ga_2I_6^{2-}$. Impure samples of $(Me_4N)_2Ga_2I_6$ were also prepared from $(Me_4N)_2Ga_2X_6$ (X = Cl or Br) by shaking solutions of the latter in nitromethane with an excess of finely powdered solid KI. The precipitated KCl or KBr was removed by filtration and the product gave pale yellow crystals on evaporation *in vacuo*. The impurities were small amounts of the mixed halide ions $Ga_2(I,X)_6^{2-}$, which were difficult to remove but were readily detected in Raman spectra by their characteristic and intense ν(Ga–Ga) and ν(Ga–I) bands in the range 120—170 cm^{-1}.

Spectroscopy.—Far i.r. spectra were recorded as petroleum jelly mulls between Polythene plates, from 500—200 cm^{-1} on a Grubb-Parsons DM4 spectrophotometer, and below 200 cm^{-1} on a Grubb-Parsons/N.P.L. 'Cube' interferometer. Solution spectra (500—200 cm^{-1}) were recorded in high density Polythene cells of 0·2 mm path length. I.r. spectra in the range 4000—400 cm^{-1} were run on a Shimadzu IR27G spectrometer and consisted of known bands of the alkylammonium cations in the compounds under study. The laser Raman spectra were scanned from 20 to 500 cm^{-1} on a Coderg PH1 spectrometer with O.I.P. 181E helium–neon excitation (632·8 nm), and on a Spex 1401 spectrometer with R.C.A. LD2140 argon ion excitation (488·0 and 514·5 nm). Frequencies are accurate to ±2 cm^{-1} except where bands are broad.

Slight frequency changes are observed on changing the cation, R_4N^+ (where R = Me, Et, Pr^n, or Bu^n). Raman and i.r. spectra of $Ga_2Cl_6^{2-}$ and $Ga_2Br_6^{2-}$ with the various cations are available in Supplementary Publication No. SUP 20671 (3 pp.).†

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† For details see Notice to Authors No. 7, in *J. Chem. Soc.* (*A*), 1970, Issue No. 20, (items less than 10 pp. are sent as full size copies).

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RESULTS AND DISCUSSION

The Ions $Ga_2X_6^{2-}$ ($X = Cl$, Br, *or* I).—The constitution of the salts $(R_4N)_2Ga_2X_6$ has been firmly established.[2,3] In the $Ga_2Cl_6^{2-}$ ion there is a covalent bond between the pair of gallium atoms, and three chlorine atoms complete an approximately tetrahedral arrangement around each gallium. The anion adopts the staggered configuration (D_{3d} symmetry) in the crystal examined by *X*-ray diffraction,[3] and the vibrational spectra (Table 1) strongly suggest that this structure is common to all the compounds and exists in both solution and solid states. Support for the attribution of the $Ga_2I_6^{2-}$ spectrum is provided by the recent Raman evidence for this ion in the sub-iodide, Ga_4I_6, where bands are observed at 124vs, 186w, and 292s cm^{-1}.[6]

TABLE 1

Vibrational spectra of $Ga_2X_6^{2-}$ ions [a]

$Ga_2Cl_6^{2-}$	$Ga_2Br_6^{2-}$	$Ga_2I_6^{2-}$	Assignment
Raman	Raman	Raman	
375m, $\rho = 0.3$ [b]	316m, $\rho = 0.6$	285s, $\rho = 0.6$	a_{1g} out-of-phase stretch
314w, depol	228m, 236sh, depol	184m, 190sh, depol	e_g Ga–X stretch
233vvs, $\rho = 0.1$	164vvs, $\rho = 0.1$	118vvs, $\rho = 0.1$	a_{1g} in-phase stretch
146ms, depol	102s	84m	e_g GaGaX bend
116s, depol	84s	75s	e_g XGaX bend
106sh, pol?	70m	42s, 48sh	a_{1g} XGaX bend
59w	32w		Lattice mode
I.r.	I.r.	I.r.	
327vs	228sh, 237vs	200vs	e_u Ga–X stretch
302s	201s	155s	a_{2u} Ga–X stretch
151s	110s	88s	a_{2u} XGaX stretch
141s	92m	74s	e_u XGaX bend
	73m		Lattice mode
89 81 76 66 m,br	64m	(50) [c]	e_u GaGaX bend

[a] Me_4N^+ salt, scanned from 20—400 cm^{-1} as crystalline solid (Raman) or petroleum jelly mull (i.r.). [b] Depolarisation ratios in nitromethane solution. [c] Estimated value.

The vibrational representation for a $Ga_2X_6^{2-}$ ion, having D_{3d} symmetry, is:

$$3a_{1g} + 3e_g + a_{1u} + 2a_{2u} + 3e_u$$

The modes of a_{1g} and e_g species are Raman active and those of a_{2u} and e_u are i.r. active. The a_{1u} mode is the inactive torsional mode. In terms of internal co-ordinates the a_{1g} modes may be described as ν(Ga–Ga), ν(Ga–X), and δ(GaX_3), although as is shown later the actual modes are extensively mixed. The e_g modes are ν(Ga–X), δ(GaX_3), and GaX_3 rocking. The a_{2u} and e_u modes which constitute the i.r. spectrum are antisymmetric counterparts of the Ga–X and GaX_3-modes in the Raman spectrum and may be expected to have somewhat similar frequencies.

Assignment of the a_{1g} *and* e_g *Modes.*—In the Raman spectra one totally symmetric (a_{1g}) mode is clearly identified by the very high intensity and strongly polarised state of the band, and a second, less intense band is polarised and so also of a_{1g} species. The frequencies of these two bands, 233 and 375 cm^{-1} of $Ga_2Cl_6^{2-}$, 164 and 316 cm^{-1} of $Ga_2Br_6^{2-}$, and 118 and 285 cm^{-1} of $Ga_2I_6^{2-}$, change appreciably from one halogen to the next, suggesting that the Ga–Ga and Ga–X stretching modes are strongly coupled. The e_g (Ga–X stretching) mode lies between these two a_{1g} frequencies, and close to the position of the i.r. active a_{2u} and e_u stretching modes. Splitting of the e_g band in some solid state Raman spectra is probably due to lifting of the degeneracy.

The expected three deformation modes (a_{1g} and $2e_g$) are observed; two being almost coincident in some spectra. The least certain feature of the assignment concerns the choice from amongst these of the a_{1g} GaX_3 deformation mode. Depolarisation measurements in solution were inconclusive, although in the spectrum of $Ga_2Cl_6^{2-}$ the band of lowest frequency appeared to be weakly polarised and so of a_{1g} species. Assignment on this basis gave the best fit between observed frequencies and those calculated by normal-co-ordinate analysis (see below). In the spectra of $Ga_2Br_6^{2-}$ and $Ga_2I_6^{2-}$ however it remains an open question which of the two lowest frequencies is the a_{1g} mode.

With the present assignments the Raman spectra of the hexahalogenodigallate ions exhibit a pattern which corresponds well with those of structurally related molecules C_2F_6,[10] Si_2X_6 ($X = Cl$, Br, or I),[11,12] and M_2Me_6 ($M = Si$, Ge, or Sn),[13,14] for which the frequency order is generally $a_{1g} \approx e_g < e_g < a_{1g} < e_g < a_{1g}$. The Raman spectrum of Ge_2Br_6[15] (isoelectronic with $Ga_2Br_6^{2-}$) has been assigned differently as regards the highest two frequencies, *i.e.* 68 (e_g), 78 (a_{1g}), 111 (e_g), 196 (a_{1g}), 315 (a_{1g}), 339 (e_g). However the depolarisation ratios of the bands in question were not very conclusive.[16]

Assignment of the a_{2u} *and* e_u *Modes.*—Two stretching and three deformation modes are predicted in the i.r. spectra. The two stretching modes (a_{2u} and e_u) are clearly observed and show small shifts with change of cation in the solid spectra. Solution i.r. spectra were not available below 200 cm^{-1} so that the solid state spectra have to be used to identify the three deformations, and the presence of lattice modes complicates the situation. One mode (assigned to a_{2u} species) is at 151 cm^{-1} in $Ga_2Cl_6^{2-}$, 110 cm^{-1} in $Ga_2Br_6^{2-}$, and 88 cm^{-1} in $Ga_2I_6^{2-}$. The e_u modes are expected by comparison with other D_{3d} molecules [10-14] to lie at lower frequencies. The assignments in Table 1 are derived from a comparison of the low frequency spectra of the various $Ga_2X_6^{2-}$ salts, and supported by the normal-co-ordinate analysis which follows.

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Normal-co-ordinate Calculations.—The Wilson *FG* matrix method[17,18] was used. After some preliminary calculations on the $Ga_2Cl_6^{2-}$ ion, in which all the angles were assumed to be tetrahedral, the *G* matrix was altered to take account of the actual structural parameters given in Table 2a. Frequencies were computed by standard methods[18] in which a set of force constants was refined to give a least-squares fit of the observed frequencies. For uniformity all the force constants are expressed in the same units (N m^{-1}) by dividing the angle bending constants by r^2 and the interaction constants by r or r^2 where appropriate.

Simple Valence Force Field.—The main aim of S.V.F.F. calculations was to test the assignment of fundamental frequencies in $Ga_2Cl_6^{2-}$. In one series (A) we assigned the Raman bands (a_{1g} and e_g species) in various ways, computed the two stretching and two bending force constants of the S.V.F.F. which gave a satisfactory set of calculated frequencies, and used these force constants to predict the i.r. active a_{2u} and e_u frequencies. The result which gave the closest agreement with observed frequencies is in Table 2b. To provide a check the procedure was reversed and the force constants derived from various choices of the i.r. assignment were used to calculate the Raman frequencies (B). The preferences for series (A) and (B) match exactly. This particular assignment is also the one preferred on experimental grounds, admittedly weak in places, and so helps to put the assignment of the $Ga_2Cl_6^{2-}$ spectrum on a firm basis. The S.V.F.F. force constants in Table 2c are in satisfactory agreement with those for the more general force field.

TABLE 2

(*a*) Structural parameters for $Ga_2Cl_6^{2-\,a}$

R = Ga–Ga distance = 239 pm, r = Ga–Cl distance = 219·6 pm, α = Cl–$\widehat{\text{Ga}}$–Cl = 104·6°, β = Ga–$\widehat{\text{Ga}}$–Cl = 113·9°

(*b*) Observed[a] and calculated frequencies/cm^{-1}

	$\nu_1(a_{1g})$	$\nu_2(a_{1g})$	$\nu_3(a_{1g})$	$\nu_4(e_g)$	$\nu_5(e_g)$	$\nu_6(e_g)$	$\nu_8(a_{2u})$	$\nu_9(a_{2u})$	$\nu_{10}(e_u)$	$\nu_{11}(e_u)$	$\nu_{12}(e_u)$
Observed[a]	375	233	106	314	146	116	302	151	327	141	76
S.V.F.F. calc. (A)	377	217	102	323	138	116	273	152	307	129	74
S.V.F.F. calc. (B)	386	230	104	351	154	122	294	156	333	141	80
G.V.F.F. calc.	375	233	106	317	149	120	303	151	323	138	72

(*c*) Valence field force constants[b]/N m^{-1})

	f_R	f_r	f_α	f_β	f_{Rr}	$f_{R\alpha} - f_{R\beta}$	$f_{r\beta}$	$f_{\alpha\alpha}$	$f_{\alpha\beta}$
G.V.F.F.	216·6	132·6	5·7	13·2	8·9	−1·2	8·5	−5·6	−3·9
S.V.F.F. (A)	210	116	12	10					
S.V.F.F. (B)	(210)	137	14	12					

[a] In crystalline $(Me_4N)_2Ga_2Cl_6$. [b] Interactions refer to adjacent bonds and angles.

General Valence Force Field.—A general valence force field for X_2Y_6 molecules[19] requires twelve force constants in all. With only eleven observed frequencies ten is the maximum permissible number of constants unless constraints are applied. Our initial approach was to exclude those interaction constants which had been shown to be small in a previous treatment[19] of molecules of this symmetry, and we omitted in turn (i) $f_{r\alpha}$ and $f_{\beta\beta}$, (ii) f_{rr} and $f_{\beta\beta}$, and f_{rr} and $f_{r\alpha}$. Methods[20,21] are available to single out badly defined force constants and a comparison of cases (i)—(iii) showed that $f_{\beta\beta}$ was in this category, and so is best constrained to zero.

Both the fields (i) and (ii) gave convergent sets of force constants which led to similar calculated frequencies in close agreement with observation. When $f_{r\alpha}$ was omitted f_{rr} assumed the value −0·023 N m^{-1}, whereas when f_{rr} was left out $f_{r\alpha}$ was 0·027 N m^{-1}. All the other force constants and interaction constants changed by less than ±0·1 N m^{-1}. We concluded that f_{rr} and $f_{r\alpha}$ were so small that both could safely be omitted along with $f_{\beta\beta}$ and that the force field of $Ga_2Cl_6^{2-}$ is adequately described by the four valence force constants and five interaction constants in Table 2c which reproduce the observed frequencies to within experimental error.

The force constant of metal–metal stretching, f_R = 216·6 N m^{-1}, is outside the range of 60 to 190 N m^{-1} for dinuclear M–M bonded species of Zn, Cd, Hg, Ge, Sn, and Pb given by Ware.[9] It may also be compared with the constants derived for the germanium–germanium bond of 160 N m^{-1} in digermane[22] and 154 N m^{-1} in hexamethyldigermane.[14] A comparison of $Ga_2Cl_6^{2-}$ with the isoelectronic molecule Ge_2Cl_6 would be of particular interest but spectra of the latter have not been reported.

It is common practice to transfer force constants from one molecule to another and the present Ga–Cl stretching force constant, f_r = 132·6 N m^{-1}, should be compared with that of the tetrachlorogallate(III) ion. The S.V.F.F. constant given by the symmetric stretching frequency of $GaCl_4^-$, ν_1, (a_1) = 346 cm^{-1}, is 250 N m^{-1}.[23] Smaller values, around 200 N m^{-1}, are deduced from G.V.F.F. calculations,[24] but even so there is a con-

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siderable discrepancy. It is tempting to attribute this difference to a weaker Ga–Cl bond in the hexachlorodigallate(II) ion, however we hesitate to draw this conclusion since the Ga–Cl bond lengths are practically the same at 219 pm in $GaCl_4^-$ [25] and 219·6 pm in $Ga_2Cl_6^{2-}$.[3] Comparing $Ga_2Cl_6^{2-}$ with the halogen-bridged molecule Ga_2Cl_6, we find that the Ga–Cl force constant in the ion lies well below the value calculated for terminal Ga–Cl bonds in Ga_2Cl_6.[26,27] The force field of the latter does not require a Ga–Ga stretching constant.[26]

TABLE 3

Normal-co-ordinate vectors for $Ga_2Cl_6^{2-}$ (L matrix elements)

(*a*) Non-degenerate modes

		Q_1	Q_2	Q_3	Q_8	Q_9	Internal co-ordinates
	ν_i	375	233	106	302	151	
	S_1	−0·1335	0·1313	−0·0142			r
a_{1g}	S_2	0·3088	0·1018	−0·2208			α, β
	S_3	0·1586	0·0552	0·0216			R
a_{2u}	S_8				0·1819	0·0466	r
	S_9				−0·2195	0·3260	α, β

(*b*) Degenerate modes

		Q_4	Q_5	Q_6	Q_{10}	Q_{11}	Q_{12}	Internal co-ordinates
	ν_i	314	146	116	327	141	75	
	S_4	−0·2146	0·0071	−0·0078				r
e_g	S_5	−0·1170	0·0550	0·2819				α
	S_6	0·2281	0·2891	−0·1133				β
	S_{10}				0·2139	−0·0200	−0·0060	r
e_u	S_{11}				0·1302	0·2620	−0·1031	α
	S_{12}				−0·0255	0·0975	0·1561	β

The present force field can be used to estimate the amount of mixing of vibrational modes. In Table 3 we give the elements of the L matrix which, according to $S = LQ$, show the extent to which each symmetry co-ordinate, S, contributes to the normal co-ordinates, Q, of a particularly symmetry species. Since the symmetry co-ordinates are previously defined [11] in terms of changes in the internal co-ordinates r, R, α, and β, Table **3** provides the basis for the approximate description of modes which accompanies the $Ga_2Cl_6^{2-}$ assignment in Table 1. All three a_{1g} modes are extensively mixed, in line with the situation in Si_2Cl_6.[11,12] To explain the large difference in intensity between ν_1 and ν_2 we note that the more intense band (ν_2) corresponds to simultaneous elongation of metal–metal and metal–chlorine bonds while the other, (ν_1), involves out-of-phase motions such that the associated polarisability changes will tend to cancel out.

In line with the strong mixing of ν_1, ν_2, and ν_3, the values for appropriate force constants are to some extent interdependent. While we believe that our finding of an unexpectedly large metal–metal stretching force constant, and a small value for Ga–Cl stretching, is reliable it is desirable to investigate the force fields of the $Ga_2X_6^{2-}$ ions more fully. An *X*-ray crystallographic study of a $Ga_2Br_6^{2-}$ salt is in progress, the results of which will allow us to extend normal co-ordinate analysis to this ion.

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