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SYNTHESIS OF ALKYLGALLIUM DIIODIDES

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Summary

Alkylgallium diiodides ($RGaI_2$, R = Me, Et, n-Pr, n-Bu) may be conveniently synthesised either by the direct reaction between gallium metal, iodine and alkyl iodide or by the reaction of "gallium monoiodide" with alkyl iodide at room temperature. Vibrational and mass spectra are also reported.

Introduction

There are very few references in the literature to the preparation and properties of alkylgallium diiodides, in marked contrast to the corresponding, chlorides and bromides. The only reported compound is $(MeGaI_2)_2$, which was prepared by the reaction between trimethylgallium and iodine [1].

Recently we synthesised analogous indium compounds by the oxidative addition of InI with RX [2]. This route is not immediately applicable to the gallium series since gallium iodide is difficult to prepare and purify.

We have previously synthesised compounds containing gallium—carbon bonds using the method of oxidation of Ga^I by alkyl halide, e.g. $Ga_2I_4 + MeI \rightarrow MeGa_2I_5$ [3]. This method is not generally applicable since the presence of the strong Lewis acid GaI_3 causes further reaction with excess alkyl halide to give polymeric species. Also, we have found that gallium metal will react with alkyl halides RI (R = Me, Et, n-Pr, n-Bu) to give products of composition $R_3Ga_2I_3$ [4, 5] and that these are not attacked by alkyl halide.

The present work was directed towards devising simple synthetic methods for the compounds $(RGaI_2)_2$, and two such methods we found involving modifications of the methods described above.

Results and discussion

Two useful methods of synthesis were used.

(1). Samples of composition GaI were obtained by weighing out stoichio-

metric quantities of gallium and iodine in vacuo at 250°C in a furnace for 24 h. These samples contained some metallic gallium together with other lower valent species of which Ga_2I_3 and Ga_2I_4 could be identified by their characteristic Raman spectra. These samples are referred to as 'GaI'. Reaction mixtures were made up by condensing dry excess alkyl iodide on to the 'GaI' sample in vacuo. They were then shaken mechanically at room temperature until all the halide and excess metal had completely reacted. This normally took between one and two weeks. In the methyl and ethyl iodide reactions pure products were obtained by the complete removal of excess alkyl iodide by vacuum distillation. For the n-propyl and n-butyl iodide reactions approximately 50% of the excess alkyl iodide was removed and the solution allowed to crystallise at −20°C. The excess alkyl iodide was then poured off and the final traces removed by distillation.

The reaction may be represented:

$$\text{'GaI'} + \text{RI} \rightarrow \text{RGaI}_2 \ (\text{R} = \text{Me, Et, n-Pr, n-Bu}) \qquad (1)$$

(2). The second method used involved the direct reaction between gallium metal, iodine and excess alkyl iodide.

Excess alkyl iodide was condensed on to a stoichiometric mixture of gallium metal and iodine in vacuo and mechanically shaken at room temperature. The iodine rapidly dissolved and the yellow solution decolourised after about half an hour. The gallium metal slowly reacted over a period of 1-2 weeks and pure products were obtained by the methods described in [1]. This is clearly the better method since the tedious preparation of 'GaI' is avoided.

In order to determine which gallium halide is initially formed in solution separate experiments were carried out in which the reactions were stopped immediately when all the iodine had been consumed, i.e. when the solutions became colourless. On removal of the solvent yellow iodide remained and this was identified as gallium(III) iodide by chemical analysis and Raman spectrum. It appears then that the gallium(III) iodide formed in this initial process undergoes redistribution reactions with the sesquihalides formed by the separate metal reactions, i.e.,

$$Ga_2I_6 + 2Ga_2I_3R_3 \rightarrow 3\ R_2Ga_2I_4 \qquad (2)$$

Vibrational spectra

These have not previously been reported and are given in Table 1. They are comparable with those reported by us for the analogous $RInI_2$ compounds [2] and are consistent with a dimeric formulation. The spectra in the gallium—iodine region are related to that of the parent compound Ga_2I_6 which above 100 cm^{-1} contains a very strong band at 143 cm^{-1}, due essentially to a bridging vibration, and a medium band at 229 cm^{-1} associated mainly with terminal Ga—I stretching [6]. Each of the iodide compounds contain a strong band in the region 154-168 cm^{-1} which may be assigned to the bridging mode. In addition bands between 211-227 cm^{-1} we assign to terminal modes.

The Raman and IR spectra of both the methyl and ethyl compounds contain single bands in the gallium—carbon region and it is seen in Table 2 that ν(Ga—C) decreases in the expected order $Cl > Br > I$.

TABLE 1

VIBRATIONAL SPECTRA OF ALKYLGALLIUM DIIODIDES (cm^{-1})[a]

Compound	ν(Ga—C)		ν(Ga—I) Raman
	Raman	IR	
$MeGaI_2$	582 m	572 s	231 m 169 s
$EtGaI_2$	550 m	546 s	211 m 164 s 289 w
n-$PrGaI_2$	623 m(br) 550 w(br)	624 s(br) 546 s(br)	218 m 160 s 197 w
n-$BuGaI_2$	629 m(br) 552 m(br)	624 m(br) 544 m(br)	227 m 154 s

[a] Raman spectra were recorded on solid samples; IR spectra were recorded on Nujol mulls.

TABLE 2

GALLIUM—CARBON STRETCHING VIBRATIONS (cm^{-1}) FOR $RGaX_2$

R	X		
	Cl[a]	Br[a]	I
Me	603	595	580
Et	568	562	549

[a] Ref. 3

TABLE 3

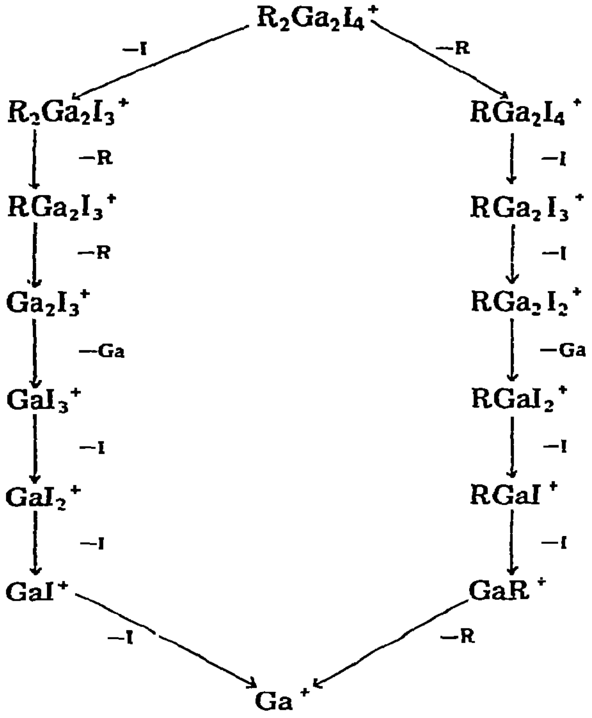
ANALYTICAL DATA OF $R_2Ga_2I_4$

Compound	Analysis found (calcd.) (%)		M.p. (°C)
	Ga	I	
$Me_2Ga_2I_4$	20.65 (20.59)	74.53 (74.96)	74-75
$Et_2Ga_2I_4$	19.90 (19.77)	71.84 (71.99)	64-66
n-$Pr_2Ga_2I_4$	19.19 (19.02)	68.84 (69.24)	22-23
n-$Bu_2Ga_2I_4$	18 67 (18.32)	66.69 (66.69)	12-13

For the n-propyl and n-butyl compounds two strong bands are observed in the metal—carbon region for each compound. These are analogous to the bands found for the corresponding indium compounds [2] and we propose that these are also due to the presence in the crystal of mixtures of two internal tortional *trans* and *gauche* forms.

Mass spectra

All of the compounds studied have mass spectra which are consistent with a dimeric structure. Proposed fragmentation patterns are shown below.



Experimental

The alkyl halides were purified by the method previously described [3]; all reactions were carried out in vacuo. IR and Raman spectra were recorded on Perkin—Elmer 225 and Carey 81 spectrometers respectively.

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References

1 G.E. Coates, M.L.H. Green and K. Wade, Organometallic Compounds, Vol. 1, Methuen, London, 1967.
2 M.J.S. Gynane, L.G. Waterworth and I.J. Worrall, J. Organometal. Chem., 43 (1972) 257.
3 W. Lind and I.J. Worrall, J. Organometal. Chem., 40 (1972) 35.
4 M.J.S. Gynane and I.J. Worrall, J. Organometal. Chem., 40 (1972) C59.
5 Unpublished work.
6 I.R. Beattie, T. Gilson and G.A. Ozin, J. Chem. Soc., (1968) 813.