

592. *Trimethylgallium. Part VI.<sup>1</sup> The Infrared Spectra and Phase Transitions of the Dimethylamino-derivatives of Dimethyl-aluminium, -gallium, and -indium*

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The aminogallium compound,  $\text{Me}_2\text{Ga}\cdot\text{NMe}_2$ , is dimeric both in benzene solution and as vapour, and is probably dimeric in the crystalline state also. The infrared spectra of the series,  $\text{Me}_2\text{M}\cdot\text{NMe}_2$  ( $\text{M} = \text{Al}, \text{Ga}, \text{and In}$ ), have been interpreted with the help of isotopic substitution. The three compounds each have crystalline and glassy forms, the latter believed to consist of cyclic oligomers or polymers. The thermodynamics of the phase transitions, crystal-to-glass transitions, and "melting" of the glass, are discussed. The infrared spectrum of the glassy form of  $\text{Me}_2\text{Ga}\cdot\text{N}(\text{CD}_3)_2$  is recorded.

SEVERAL years ago the vapours of the dimethylamino-derivatives,  $\text{Me}_2\text{N}\cdot\text{MMe}_2$  ( $\text{M} = \text{Al},^2 \text{Ga},^3 \text{and In}^4$ ), were shown to consist of dimeric species  $(\text{Me}_2\text{N}\cdot\text{MMe}_2)_2$ . However, the vapour pressure-temperature plots ( $\log p$  against  $T^{-1}$ ) for the three compounds have discontinuities at about  $50^\circ$  (Al),  $70^\circ$  (Ga), and  $75^\circ$  (In). The gallium and indium compounds were described as dimorphic in that crystals forming from the vapour at or near room temperature have sharply defined faces and angles, but material condensing about  $70\text{--}80^\circ$  appears as of dendritic habit with a strong tendency to form rounded edges. The high temperature modifications of all three compounds are glassy and non-crystalline, as shown by their loss of anisotropy, when heated above the transition region and viewed with polarised light by means of a hot-stage microscope, and by the flow observed when the glass is deformed mechanically. We now suggest that the crystalline and glassy forms have different molecular structures, infrared-spectroscopic evidence in favour of this conclusion being described below.

The aluminium, gallium, and indium compounds have very similar properties and although the spectra of all three are described, only the gallium compound was selected for a study of molecular complexity. The degree of association of  $\text{Me}_2\text{Ga}\cdot\text{NMe}_2$ , measured cryoscopically in 0.378 and 0.756 molal solutions in benzene, is 2.02, 2.11. The earlier finding that the vapours of all three compounds are dimeric at pressures in the range of tens to hundreds of millimetres has now been supplemented by a mass-spectroscopic study of the vapour evaporating from the gallium compound at room temperature; the dimer is the predominant species also at very low pressure. A preliminary single-crystal X-ray analysis (by Dr. H. M. M. Shearer and Miss C. R. Letts of this department) of the low-temperature modification has shown that the monoclinic crystals have unit-cell dimensions  $a = 7.63$ ,  $b = 8.12$ ,  $c = 12.76 \text{ \AA}$ ,  $\beta = 117^\circ 30'$ , the space group being  $P2_1/c$ . These data are consistent with the presence of two dimer molecules or four monomers in the unit cell; a polymeric structure appears unlikely. Since the state of association in the crystal is likely to be at least as great as in the vapour, we conclude at present that the crystal consists of dimer molecules. A detailed analysis will be reported later.

The infrared absorptions of the dimethylamino- and the di- $[\text{}^2\text{H}_3]$ methylamino-compounds (*e.g.*,  $[\text{Me}_2\text{Ga}\cdot\text{N}(\text{CD}_3)_2]_2$ ) are listed in Table I, the spectra of the two dimethylgallium compounds being shown in Figures 1a and b. The spectra of the aluminium and gallium compounds in the vapour phase were also recorded, using a heated cell, but did not differ appreciably from the spectra of solutions in Nujol. The absorptions due to the dimethylmetal groups were assigned by comparison with the spectra of the dimethylphosphino- and -arsino-compounds,<sup>1</sup> and by reference to the spectra of other compounds

<sup>1</sup> Part V, O. T. Beachley and G. E. Coates, preceding Paper.

<sup>2</sup> N. Davidson and H. C. Brown, *J. Amer. Chem. Soc.*, 1942, **64**, 316.

<sup>3</sup> G. E. Coates, *J.*, 1951, 2003.

<sup>4</sup> G. E. Coates and R. A. Whitcombe, *J.*, 1956, 3351.

TABLE I

$(\text{Me}_2\text{Al}\cdot\text{NMe}_2)_2$			$(\text{Me}_2\text{Ga}\cdot\text{NMe}_2)_2$			$(\text{Me}_2\text{In}\cdot\text{NMe}_2)_2$			
$d_6^b$	$\nu_{\text{H}}/\nu_{\text{D}}$		$d_6^b$	$\nu_{\text{H}}/\nu_{\text{D}}$		$d_6^b$	$\nu_{\text{H}}/\nu_{\text{D}}$		
1459	—		1461	—		1468	—		N-CH <sub>3</sub> $\delta$ (antisym.)
—	1082	1·35	—	1074	1·36	—	1071	1·37	N-CD <sub>3</sub> $\delta$ (antisym.)
1438	—		1448	—		1430	—		N-CH <sub>3</sub> $\delta$ (sym.)
—	1065	1·35	—	1064	1·36	—	—		N-CD <sub>3</sub> $\delta$ (sym.)
1400	1390		1408	1399		1408	1402		M-CH <sub>3</sub> $\delta$ (antisym.)
1231	—		1231	—		1228	—		N-CH <sub>3</sub> rock
—	1060	1·16	—	1062	1·16	—	1062	1·16	N-CD <sub>3</sub> rock
1198	1200		1206	1206		1164	1162		M-CH <sub>3</sub> $\delta$ (sym.)
1163	—		1192	—		1155	—		N-CH <sub>3</sub> rock
—	956	1·22	—	957	1·25	—	941	1·23	N-CD <sub>3</sub> rock
1113	1118		1138	1131		1138	1136		C-N stretch (antisym.)
1042	1031		1049	1036		1050	1031		C-N stretch (sym.)
900	—		902	—		916, 891	—		N-CH <sub>3</sub> rock
—	800	1·13	—	804	1·12	—	809, 794	1·13, 1·12	N-CD <sub>3</sub> rock
			727	727					M-CH <sub>3</sub> rock
694 <sup>c</sup>	694 <sup>c</sup>		661	663		699	699		M-CH <sub>3</sub> rock
—	—		573	571		509	510		M-CH <sub>3</sub> stretch (antisym.)
585	578		536	533		482	481		M-CH <sub>3</sub> stretch (sym.)
508	482	1·05	498	452	1·10	443	405	1·09	M-N stretch

<sup>a</sup> Spectra between 2000—1350  $\text{cm}^{-1}$  were observed as perfluorokerosene mulls whereas those between 1350—400  $\text{cm}^{-1}$  were observed as solutions in Nujol. <sup>b</sup> Infrared spectra of  $[\text{Me}_2\text{M}\cdot\text{N}(\text{CD}_3)_2]_2$ . <sup>c</sup> This absorption is probably a combination of an aluminium-methyl rocking and the antisymmetrical stretching modes (see references 1 and 6).

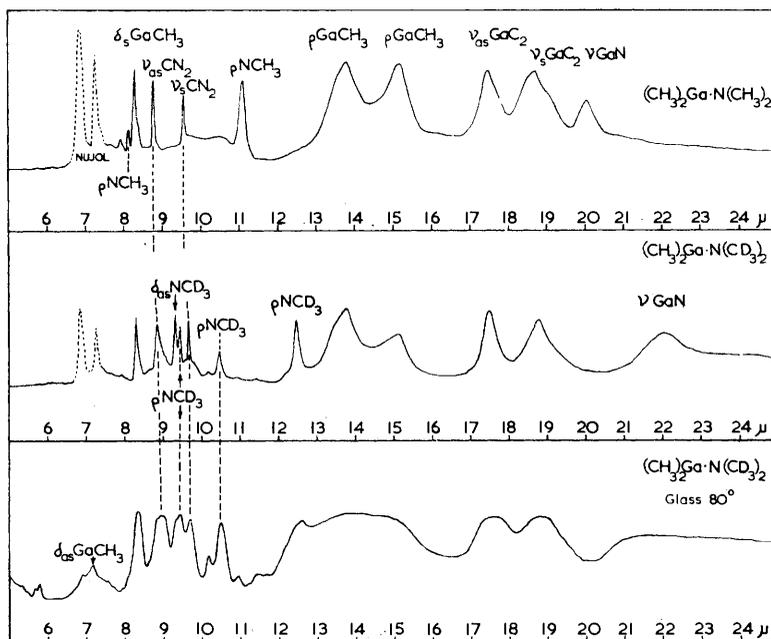


FIGURE 1

containing these groups: <sup>5,6</sup> their spectroscopic characteristics have already been discussed <sup>1</sup> and the absorptions due to the dimethylmetal group are very similar whether the group is bound to nitrogen, phosphorus, <sup>1</sup> arsenic, <sup>1</sup> oxygen, <sup>5</sup> or sulphur. <sup>5</sup>

The absorptions due to the dimethylamino-group were assigned on the basis of the

<sup>5</sup> G. E. Coates and R. N. Mukherjee, *J.*, 1964, 1295.

<sup>6</sup> A. P. Gray, *Canad. J. Chem.*, 1963, **41**, 1511.

spectra of related dimethylamino-compounds,<sup>7-9</sup> and confirmed by isotopic substitution. The antisymmetric and symmetric methyl deformation absorptions of the  $\text{NMe}_2$  groups are in the range 1459—1468 and 1430—1448  $\text{cm}^{-1}$ , respectively,  $\nu_{\text{H}}/\nu_{\text{D}}$  being about 1.36. The three absorptions due to  $\text{N-CH}_3$  rocking are in the ranges 1228—1231, 1155—1192, and 900—916  $\text{cm}^{-1}$ , and have smaller deuterium shifts of 1.16, 1.23, and 1.13, respectively, these being consistent with the assigned modes.<sup>6</sup> The absorptions in the ranges 1113—1138 and 1031—1050  $\text{cm}^{-1}$  are hardly affected by deuteration, do not therefore involve vibrations within the methyl groups, and are assigned as  $\text{NC}_2$  stretching frequencies.

The medium-intensity absorptions at 508, 498, and 443  $\text{cm}^{-1}$  are believed to be due to aluminium-, gallium-, and indium-nitrogen stretches by comparison with metal-nitrogen absorptions in the spectra of  $\text{H}_3\text{Al}\cdot\text{NMe}_3$ ,<sup>10</sup>  $\text{H}_3\text{Al}(\text{NMe}_3)_2$ ,<sup>10</sup> and  $\text{H}_3\text{Ga}\cdot\text{NMe}_3$ <sup>11</sup> (533, 460, and 482  $\text{cm}^{-1}$ , respectively). A similar absorption at 465  $\text{cm}^{-1}$ , has been observed<sup>12</sup> in the spectrum of  $(\text{Me}_2\text{Al}\cdot\text{N}\cdot\text{CMe}_2)_2$ , which presumably has a very similar  $\text{Al}_2\text{N}_2$  cyclic structure. An alternative assignment as a C-N-C or a C-C-C bending mode is rejected since these are normally at much lower frequencies. The  $\nu_{\text{H}}/\nu_{\text{D}}$  ratios for these low-frequency absorptions are perplexing, and it is doubtful if they are combination bands since no other absorptions of appreciable intensity were observed between 200 and 400  $\text{cm}^{-1}$ .

The spectrum of the glassy form of di- $[\text{}^2\text{H}_3]$ methylaminodimethylgallium, as a film between potassium bromide plates heated to 80°, is shown in Figure 1c. During the preparation of these samples the glassy material was seen to flow very slowly under the pressure exerted by the plates of the spectroscopic cell; this flow did not occur in the crystalline region below 55°. The absorptions due to the di- $[\text{}^2\text{H}_3]$ methylamino- and the dimethylgallium groups are broader than, but very close in frequency to, those observed for the dimer in Nujol solution. We believe the most significant difference between Figures 1b and c is the replacement of the absorption at 452  $\text{cm}^{-1}$  (Figure 1b) assigned to gallium-nitrogen stretching, by the very broad absorption found below 500  $\text{cm}^{-1}$  in the spectrum of the glass (Figure 1c). If the absorption at 452  $\text{cm}^{-1}$  in the  $[\text{Me}_2\text{Ga}\cdot\text{N}(\text{CD}_3)_2]_2$  molecule is due to Ga-N stretching, then the extreme broadening of this, the only truly skeletal mode of vibration of the dimer, would be entirely consistent with a transformation of the dimer to a mixture of oligomers or polymers (probably cyclic) above 55—80°.

The temperature ranges in which these compounds undergo the two reversible condensed phase transitions, crystal to glass and "melting" of the glass are given in Table 2.

TABLE 2

Compound	Transition-temperature ranges		
	Physical state at 25°	Crystal $\longrightarrow$ Glass (°c)	"Melting" of the glass (°c)
$\text{Me}_2\text{Al}\cdot\text{NMe}_2$	Crystalline	50—70	153—154 <sup>a</sup>
$\text{Me}_2\text{Ga}\cdot\text{NMe}_2$	Crystalline	55—80	157—161
$\text{Me}_2\text{In}\cdot\text{NMe}_2$	Crystalline	70—80	174—175

<sup>a</sup> Lit.,<sup>2</sup> 154—156°.

It is of interest that the glassy form of, for example,  $\text{Me}_2\text{Ga}\cdot\text{NMe}_2$  may be cooled to 20° (well below the transition temperature range) without crystallisation taking place; this can readily be observed when the glassy material condenses from the vapour inside a glass bulb forming transparent circles of *ca.* 1 cm. diameter. Application of a fragment of solid carbon dioxide to the outside of the vessel for a moment results in crystallisation of the entire ring during a second or two.

<sup>7</sup> J. R. Barcelo and J. Bellanato, *Spectrochim. Acta*, 1956, **8**, 27.

<sup>8</sup> A. J. Banister, N. N. Greenwood, B. P. Straughan, and J. Walker, *J.*, 1964, 995.

<sup>9</sup> R. L. Amster and R. C. Taylor, *Spectrochim. Acta*, 1964, **20**, 1487.

<sup>10</sup> G. W. Fraser, N. N. Greenwood, and B. P. Straughan, *J.*, 1963, 3742.

<sup>11</sup> N. N. Greenwood, A. Storr, and M. G. H. Wallbridge, *Inorg. Chem.*, 1963, **2**, 1036; D. F. Shriver, R. L. Amster, and R. C. Taylor, *J. Amer. Chem. Soc.*, 1962, **84**, 1321.

<sup>12</sup> J. E. Lloyd and K. Wade, unpublished observation.

As a working hypothesis we assume that the solid and the volatile mobile liquid consist only of dimers,  $X_2$ , and that the glass is a polymer,  $X_n$ . The stable state changes from solid to glass to liquid as the temperature is raised and the free energies could therefore vary as shown in Figure 2a. Since the rate of decrease of  $G^0$  with increasing temperature follows the sequence solid < glass < liquid, the enthalpies and entropies of the three species must also increase in this order, as indicated qualitatively in Figure 2b. This applies for any variation of the  $G^0$ 's with temperature which is consistent with the observations.

The transition from glass to liquid occurs homogeneously over a range of only a few degrees, showing that the equilibrium constant for this process must have a large temperature coefficient and, hence, that the difference between the enthalpies of the two species must also be relatively large. This is qualitatively consistent with a liquid composed of cyclic dimers (planar four-membered rings) which must be strained at least at the nitrogen atom, and a glass which is highly polymeric and free from strain. The additional strain

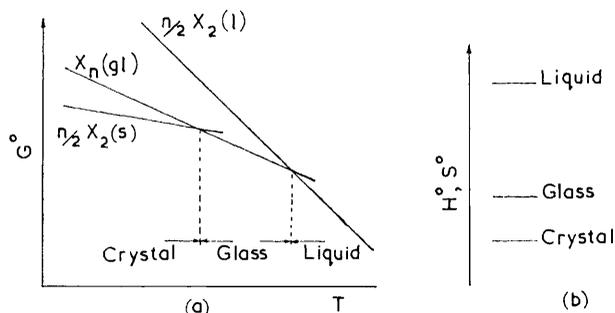


FIGURE 2

energy required in the formation of  $n/2$  moles of dimer from 1 mole of  $n$ -mer would then account for the large difference between the enthalpies of glass and liquid required by the observations.\*

The co-ordinate bonds result in appreciable charges on alternate atoms (metal and nitrogen), and the evidently low enthalpy and entropy of the solid (relative to the glass or liquid) may well arise from attractive electrostatic interactions in a lattice containing highly symmetrical molecules. The two possible molecular structures (monomer and dimer) deduced for the solid from preliminary X-ray analysis are both consistent with this explanation.

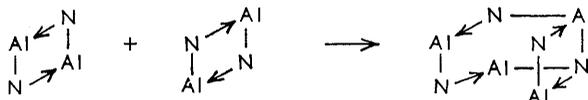
The phosphino- and arsino-compounds<sup>1</sup> (e.g.,  $\text{Me}_2\text{Al}\cdot\text{PMe}_2$ ,  $\text{Me}_2\text{Ga}\cdot\text{AsMe}_2$ ) have not been observed in crystalline forms at normal temperatures but only as glasses. These compounds are trimeric in solution, and if they are also trimeric in the crystalline state the non-planar six-membered ring would not have the high symmetry of the dimethylamino-dimer or -monomer. This could account for the lower stability (greater free energy) of the hypothetical crystalline trimer, relative to the glass.

The present observations could be of interest in connection with problems of the thermodynamics and kinetics of polymerisation, particularly since the polymerisation

\* The heat of polymerisation of cyclobutane<sup>13</sup> shows that the strain energy of a carbon atom in the four-membered ring is ca. 6 kcal. per g.-atom. If the strain energy at the nitrogen atom in the present dimers is similar, this factor would contribute ca. 60 kcal. to the change in enthalpy on the formation of five moles of dimer from one mole of decamer; the strain energy of the heavier metal atom is neglected in comparison. This is already sufficient to account for the change from glass to liquid over a small temperature interval if the equilibrium mixture containing equal weights of decamer and dimer appears as a glass or highly viscous liquid, and as a mobile liquid when the decamer : dimer ratio is 1 : 2 (by weight).

<sup>13</sup> F. S. Dainton and K. J. Ivin, *Quart. Rev.*, 1958, **12**, 61.

consists, beyond reasonable doubt, simply of the replacement of one co-ordinated ligand by another; *e.g.*,



Other polymerisations<sup>13</sup> (*e.g.*, that of sulphur) displaying floor and ceiling temperatures involve reactive intermediates such as radicals or ions.

#### EXPERIMENTAL

All of the compounds studied are air- and moisture-sensitive and were handled in a vacuum or under an atmosphere of purified nitrogen. The compounds were prepared by the pyrolysis of the dimethylamine adduct of trimethyl-aluminium, -gallium, and -indium by previously described methods. Infrared spectra were recorded on a Grubb-Parsons Spectromaster prism-grating spectrometer.

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