

Dialkyl(2-methylimidazolyl)metal Tetramers of Group III Elements: Crystal and Molecular Structure of Tetrakis- μ -(2-methylimidazolyl)-tetrakis(diethylgallium)

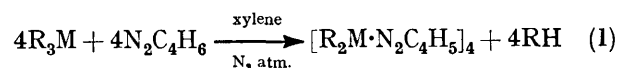
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A series of compounds $[R_2ML]_4$ ($R = \text{Me}$, $M = \text{B}$, Al , Ga , and In ; $R = \text{Et}$, $M = \text{Ga}$; $L = 2\text{-methylimidazolyl}$) has been synthesized by reaction of Group III metal trialkyls with molar equivalents of 2-methylimidazole. The products have been characterized and the X-ray crystal structure of the Et_2Ga derivative determined. Crystals are monoclinic, $a = 15.31(2)$, $b = 19.39(3)$, $c = 14.21(2)$ Å, $\beta = 101.30(9)^\circ$, space group $I2/a$, $Z = 4$ (tetrameric units). The structure was determined from diffractometer data by Patterson and Fourier methods, and refined by full-matrix least-squares methods to R 0.101 for 1 182 observed reflexions. The molecule consists of four diethylgallium moieties linked by 2-methylimidazolyl rings to form a 'square' of side 6 Å. The molecule has pseudo- D_{2d} symmetry and crystallographic two-fold symmetry, the two-fold axis passing through two of the gallium atoms. Mean dimensions are: Ga-N 1.98, Ga-C 1.90, N-C 1.36, C-CH₃ 1.46 Å; N-Ga-N 102, C-Ga-C 124, and N-Ga-C 107°.

THE reaction of Group III trialkyls with ligands containing acidic hydrogen yields adducts which eliminate alkanes under appropriate conditions producing coordinatively unsaturated intermediates.¹ Co-ordinative saturation can be achieved by multiple bonding, chain polymerization, or cyclization. In the majority of cases cyclization occurs to give di- or tri-meric species, the actual degree of association being determined by a balance between steric effects, valency-angle strain, entropy, and the nature of the intermediates involved in the reaction.^{1,2} We now extend previous studies^{3,4} to

on the polymeric imidazolylthallium dimethyl compound.⁶

The present compounds were prepared from stoichiometric amounts of the Group III trialkyl and 2-methylimidazole in xylene [reaction (1)]. It was necessary to



use reflux conditions for all reactions, partly because of the low solubility of 2-methylimidazole in xylene at room temperature. Completion of reaction was signalled by

TABLE I
Analytical data for the tetrameric imidazolyl complexes.

Compound	M.p./°C	Analytical data (%)							
		Found				Reqd.			
		M	C	H	N	M	C	H	N
$[\text{Me}_2\text{B}(\text{N}_2\text{C}_4\text{H}_5)]_4$	308—309 *		59.2	9.0	23.2		59.1	9.0	23.2
$[\text{Me}_2\text{Al}(\text{N}_2\text{C}_4\text{H}_5)]_4$	261—262 *	19.1				19.5			
$[\text{Me}_2\text{Ga}(\text{N}_2\text{C}_4\text{H}_5)]_4$	253—254 *		39.8	6.1	15.2		39.8	6.1	15.5
$[\text{Me}_2\text{In}(\text{N}_2\text{C}_4\text{H}_5)]_4$	221—222 *		32.4	5.0	12.3		31.9	4.9	12.4
$[\text{Et}_2\text{Ga}(\text{N}_2\text{C}_4\text{H}_5)]_4$	129—130		46.0	7.3	13.2		46.0	7.2	13.4
$[\text{Me}_2\text{Ga}(\text{N}_2\text{C}_3\text{H}_3)]_x$	155—156		36.4	5.7	16.4		36.0	5.4	16.8

* Decomp.

include 2-methylimidazolyl derivatives of Group III dialkyls. Little attention has been given to this area of chemistry, except for a note on boron dialkyl derivatives of imidazole and 2-methylimidazole,⁵ and a short report

¹ G. E. Coates and K. Wade, 'Organometallic Compounds: Vol. 1, The Main Group Elements,' Methuen, London, 1967, 3rd edn., ch. 3.

² M. F. Lappert, M. K. Majumdar, and B. P. Tilley, *J. Chem. Soc. (A)*, 1966, 1590.

completion of alkane evolution and also by the lack of $\nu(\text{NH})$ in the i.r. spectrum of the final solution. When the clear xylene solution was cooled, the product was deposited as needle-like crystals. Analytical data for the compounds prepared are summarized in Table I.

³ A. Storr and B. S. Thomas, *J. Chem. Soc. (A)*, 1971, 3850.

⁴ A. Arduini and A. Storr, *J.C.S. Dalton*, 1974, 503.

⁵ S. Trofimenko, *J. Amer. Chem. Soc.*, 1967, **89**, 3903.

⁶ A. G. Lee, *J. Chem. Soc. (A)*, 1971, 880.

Of the compounds listed in Table 1 only the aluminium compound was air-sensitive, the remaining compounds being unaffected, even after prolonged exposure to the atmosphere. A similar stability for pyrazolyl derivatives of gallium dialkyls has been observed recently.^{4,7,8} In addition to the 2-methylimidazolyl derivatives, the imidazolyl compound of dimethylgallium was prepared. It was insoluble in common organic solvents, and was presumed to be polymeric like the analogous $[\text{Me}_2\text{Ti}(\text{N}_2\text{C}_3\text{H}_3)]_x$ (ref. 6) and $[\text{Et}_2\text{B}(\text{N}_2\text{C}_3\text{H}_3)]_x$ (ref. 5) compounds; a state of oligomerization was also predicted on the basis of molecular model studies. The 2-methylimidazolyl derivatives were all shown to be tetrameric, again the most favoured arrangement sterically, by mass spectral measurements, and in the case of the $[\text{Et}_2\text{Ga}(\text{N}_2\text{C}_4\text{H}_5)]_4$ compound by X-ray structural analysis. As pointed out previously for the $[\text{Et}_2\text{B}(\text{N}_2\text{C}_4\text{H}_5)]_4$ compound,⁵ molecular models indicate that the tetramers are devoid of strain, and are the only unstrained oligomers which can be constructed from the monomer unit, $\text{R}_2\text{M}(\text{N}_2\text{C}_4\text{H}_5)$.

TABLE 2
Mass spectrum of $[\text{Me}_2\text{Ga}(\text{N}_2\text{C}_4\text{H}_5)]_4$

<i>m/e</i>	Intensity	Assignment
713	4.5	
711	23.8	
709	49.7	$\text{Me}_7\text{Ga}_4(\text{N}_2\text{C}_4\text{H}_5)_4^+$
707	49.0	
705	18.9	
647	0.6	
645	3.5	
643	6.3	$\text{Me}_8\text{Ga}_4(\text{N}_2\text{C}_4\text{H}_5)_3^+$
641	6.3	
639	2.8	
531	3.8	
529	13.3	$\text{Me}_5\text{Ga}_3(\text{N}_2\text{C}_4\text{H}_5)_3^+$
527	18.2	
525	9.8	
465	4.2	
463	14.0	$\text{Me}_6\text{Ga}_3(\text{N}_2\text{C}_4\text{H}_5)_2^+$
461	22.0	
459	11.2	
349	8.4	
347	24.1	$\text{Me}_3\text{Ga}_2(\text{N}_2\text{C}_4\text{H}_5)_2^+$
345	18.2	
283	35.7	
281	100.0	$\text{Me}_4\text{Ga}_2(\text{N}_2\text{C}_4\text{H}_5)^+$
279	75.5	
253	8.0	
251	23.1	$\text{Me}_2\text{Ga}_2(\text{N}_2\text{C}_4\text{H}_5)^+$
249	17.5	
182	2.8	$\text{Me}_2\text{Ga}(\text{N}_2\text{C}_4\text{H}_5)^+$
180	4.2	
152	3.4	$\text{Ga}(\text{N}_2\text{C}_4\text{H}_5)^+$
150	4.9	
101	53.1	Me_2Ga^+
99	78.3	
71	7.0	Ga^+
69	11.0	

Mass Spectra.—The mass spectra of the air-stable compounds all showed peaks characteristic of a tetrameric species, although in most cases the parent-ion peak itself was not observed. The highest mass peaks usually corresponded to the parent ion minus one or more alkyl groups, and these were amongst the most

⁷ A. Storr, unpublished results.

⁸ K. Breakell, D. J. Patmore, and A. Storr, *J.C.S. Dalton*, 1975, 749.

intense signals. A similar absence of parent ions in the mass spectra of organo-gallium and -aluminium compounds has been noted previously.⁷⁻¹⁰

The principle features of the mass spectrum of $[\text{Me}_2\text{Ga}(\text{N}_2\text{C}_4\text{H}_5)]_4$ are listed in Table 1 together with tentative assignments. Depending upon the number of gallium atoms contained in a particular ion a characteristic multiplet is observed with individual peaks separated by two mass units. The relative intensities of the peaks within a multiplet agree well with those predicted from the isotopic distribution of the metal atoms [⁶⁹Ga (60%); ⁷¹Ga (40%)]. The mass spectra of the remaining air-stable 2-methylimidazolyl compounds were similar and again indicated a tetrameric constitution for the compounds in the gas phase.

¹H N.m.r. and I.r. Spectra.—The ¹H n.m.r. spectra (Table 3) are consistent with tetrameric species in solution. Thus, from a consideration of the molecular

TABLE 3
¹H n.m.r. data for $[\text{R}_2\text{ML}]_4$ (L = 2-methylimidazolyl) compounds

Compound		2-Methylimidazolyl moiety		$\tau(\text{M-R})$
M	R	$\tau(\text{CH})$	$\tau(\text{CH}_3)$	
B ^a	Me	3.06s	8.47s	9.71s
Ga ^a	Me	3.19s	8.51s	10.25s
In ^a	Me	3.31s	8.24s	10.01s
Ga ^b	Et	3.17s	8.32s	8.61t ($\beta\text{-CH}_2$), 9.11q ($\alpha\text{-CH}_2$)

^a In CDCl_3 solution; τ values relative to $\tau(\text{CDCl}_3)$ 2.84 p.p.m. [$\tau(\text{TMS})$ 10.00 p.p.m.]. ^b In C_6D_6 solution; τ values relative to $\tau(\text{C}_6\text{H}_6)$ 2.84 p.p.m. [$\tau(\text{TMS})$ 10.00 p.p.m.]. s = Singlet, t = triplet, q = quartet.

structure shown for $[\text{Et}_2\text{Ga}(\text{N}_2\text{C}_4\text{H}_5)]_4$ in Figure 1, and assuming a similar structure for the $[\text{Me}_2\text{M}(\text{N}_2\text{C}_4\text{H}_5)]_4$ derivatives in solution, three proton signals are to be expected: one for the two equivalent CH protons of the imidazolyl ring, one for the 2-Me protons, and one for the M-Me groups. This pattern, in the predicted intensity ratio of 2:3:6, was indeed observed for the three $[\text{Me}_2\text{M}(\text{N}_2\text{C}_4\text{H}_5)]_4$ compounds. Similarly the ¹H n.m.r. spectrum of the $[\text{Et}_2\text{Ga}(\text{N}_2\text{C}_4\text{H}_5)]_4$ compound is consistent with a tetrameric species in solution.

TABLE 4
Selected i.r. data for $[\text{R}_2\text{ML}]_4$ compounds (L = 2-methylimidazolyl)

Compound		$\nu(\text{M-C})$		Ring modes
R	M	asym	sym	
Me	B	1 066s	1 032s	585m
Me	Al	640m	585m	460m
Me	Ga	584m	546m	437m
Me	In	520m	490m	420s
Et	Ga	560m	525m	435m

s = Strong, m = medium.

Selected vibrational frequencies from the i.r. spectra of the tetramers (Nujol) are listed in Table 4. In all the spectra $\nu(\text{NH})$ of the initial 2-methylimidazole (at ca.

⁹ B. D. Chambers, G. E. Coates, F. Glockling, and M. Weston, *J. Chem. Soc. (A)*, 1969, 1712.

¹⁰ K. J. Alford, K. Gosling, and J. D. Smith, *J.C.S. Dalton*, 1972, 2203.

3300 cm^{-1}) had disappeared, indicating that complete reaction had occurred. The tentative assignments of the asymmetric and symmetric M-C stretching frequencies are made on the basis of previous assignments,¹¹⁻¹⁸ {absorption bands at lower frequencies are assigned to $\frac{1}{2}R_2M(N_2C_4H_5)_4$ ring modes}. With increasing atomic number of the Group III atom the various frequencies are observed to decrease, indicating the operation of the expected mass effect.

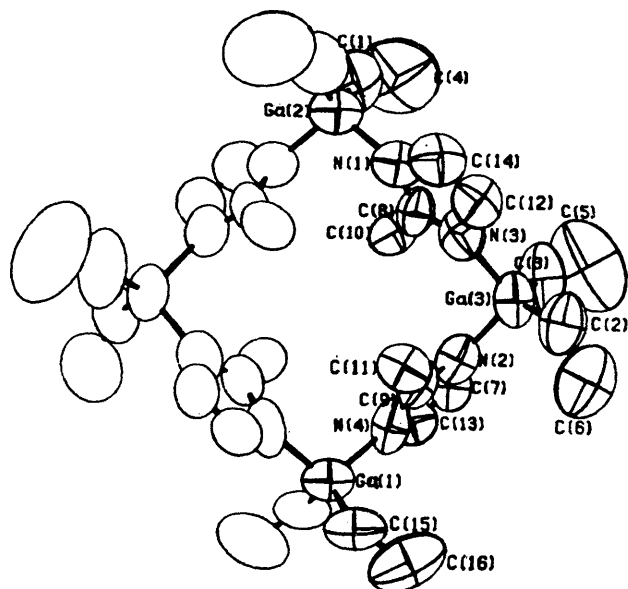


FIGURE 1 View of the $[\text{Et}_2\text{Ga}(\text{N}_2\text{C}_4\text{H}_5)_4]_4$ tetramer, with hydrogen atoms omitted for clarity

Crystal Structure of $[\text{Et}_2\text{Ga}(\text{N}_2\text{C}_4\text{H}_5)_4]_4$.—Figure 1 is a view of the tetrameric molecule; the asymmetric unit is one half a molecule. The labelled is related to the unlabelled half of the molecule by the crystallographic two-fold axis which passes through Ga(1) and Ga(2). The 'square' molecule has pseudo- D_{2d} symmetry with the four diethylgallium moieties at the 'corners' of the square. Each gallium atom is tetrahedrally co-ordinated to two ethyl groups and two nitrogen atoms (one from each of two 2-methylimidazolyl groups). The orientation of these imidazolyl rings alternates in the tetramer, with one methyl group above, and the adjacent one below the plane of the four Ga atoms, an arrangement favoured over the alternative with all four methyl groups on one side of the Ga_4 ring. The former arrangement was initially predicted from consideration of molecular models, and removes a very unfavourable $\text{C} \cdots \text{C}$ non-bonded contact of *ca.* 3.1 \AA between adjacent 2-Me groups in the alternative arrangement.

The methyl groups are all canted towards the centre of the molecules, presumably to avoid steric interaction

¹¹ A. Storr and B. S. Thomas, *Canad. J. Chem.*, 1970, **48**, 3667.

¹² W. Sawodny and J. Goubeau, *Z. phys. Chem.*, 1965, **44**, 227.

¹³ G. E. Coates and R. N. Mukherjee, *J. Chem. Soc.*, 1964, 1295.

¹⁴ O. T. Beachley and G. E. Coates, *J. Chem. Soc.*, 1965, 3241.

¹⁵ O. T. Beachley, G. E. Coates, and G. Kohnstam, *J. Chem. Soc.*, 1965, 3248.

¹⁶ J. E. Lloyd and K. Wade, *J. Chem. Soc.*, 1965, 2662.

¹⁷ J. R. Jennings and K. Wade, *J. Chem. Soc. (A)*, 1967, 1333.

with the ethyl groups on the gallium atoms. Both unique imidazolyl rings are planar. Important least-squares planes and their dihedral angles are listed in Table 5.

The mean Ga-N distance (1.98 \AA) is in good agreement with corresponding distances in other compounds containing tetrahedrally-co-ordinated gallium.¹⁹⁻²² The mean Ga-C distance (1.90 \AA) is somewhat shorter than

TABLE 5

(a) Equations of weighted best planes in the form $lX + mY + nZ = p$ where X, Y, Z are orthogonal co-ordinates in \AA . * Deviations (\AA) of atoms from the planes are given in square brackets

Plane (1): Ga(1)—(3), Ga(3')

$$0.4608X - 0.8875Z = 5.2912$$

[Ga(1) 0, Ga(2) 0, Ga(3) 0, Ga(3') 0, N(1) $-0.51(2)$, N(2) $0.54(2)$, N(3) $-0.48(2)$, N(4) $0.52(2)$, C(10) $1.49(2)$, C(11) $-1.52(2)$]

Plane (2): N(1), N(3), C(8), C(10), C(12), C(14)

$$0.7711X + 0.6301Y - 0.0921Z = 14.2156$$

[N(1) $0.00(2)$, N(3) $-0.00(2)$, C(8) $-0.01(3)$, C(10) $0.00(2)$, C(12) $0.02(3)$, C(14) $-0.01(3)$, Ga(2) $0.095(3)$, Ga(3) $0.128(3)$]

Plane (3): N(2), N(4), C(7), C(9), C(11), C(13)

$$-0.3972X + 0.6355Y - 0.6620Z = -4.4253$$

[N(2) $-0.01(2)$, N(4) $-0.01(2)$, C(7) $0.00(3)$, C(9) $0.01(3)$, C(11) $0.00(2)$, C(13) $0.01(3)$]

Plane (4): N(1'), N(3'), C(8'), C(10'), C(12'), C(14')

$$0.7711X - 0.6301Y - 0.0921Z = 3.4918$$

Plane (5): N(2'), N(4'), C(7'), C(9'), C(11'), C(13')

$$-0.3972X - 0.6355Y - 0.6620Z = -4.6975$$

(b) Dihedral angles ($^\circ$) between planes

(1)-(2)	64.1	(2)-(4)	78.1
(1)-(3)	66.1	(2)-(5)	130.2
(2)-(3)	81.1		

* $X, Y,$ and Z are derived as follows:

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} a & 0 & c \cos \beta \\ 0 & b & 0 \\ 0 & 0 & c \sin \beta \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

corresponding distances quoted for other compounds;^{21,22} however, these were for Ga-Me and not Ga-Et bonds. The N-C distances within the imidazolyl rings ($1.32-1.44$, mean 1.36 \AA) are in good agreement with those in previously studied pyrazolyl compounds.¹⁹⁻²² Mean $\text{C}(sp^2)-\text{C}(sp^2)$ distances within the five-membered rings are 1.28 , and mean $\text{C}(sp^2)-\text{CH}_3$ 1.46 \AA . The $\text{C}(sp^3)-\text{C}(sp^3)$ distances in the ethyl groups (1.29 \AA) are extremely short when compared to the usual C-C distance of 1.54 \AA and the discrepancy may be attributed to uncertainty in the true location of the atomic centres of the carbon atoms, owing to high thermal motion.

Valency angles associated with the gallium atoms fall into three categories: N-Ga-N (mean 102°), C-Ga-C (mean 124°), and N-Ga-C (mean 107°). This trend has

¹⁸ J. R. Jennings, I. Pattison, K. Wade, and B. K. Wyatt, *J. Chem. Soc. (A)*, 1967, 6108.

¹⁹ D. F. Rendle, A. Storr, and J. Trotter, *J.C.S. Dalton*, 1973, 2252.

²⁰ W. Harrison, A. Storr, and J. Trotter, *J.C.S. Dalton*, 1972, 1554.

²¹ D. F. Rendle, A. Storr, and J. Trotter, *J.C.S. Dalton*, 1975, 176; *J.C.S. Chem. Comm.*, 1974, 406.

²² D. J. Patmore, D. F. Rendle, A. Storr, and J. Trotter, *J.C.S. Dalton*, 1975, 718.

TABLE 6

Bond lengths (Å), and valency angles (°), with estimated standard deviations in parentheses

(a) Bond distances			
Ga(1)—N(4)	1.98(2)	N(3)—C(8)	1.32(4)
Ga(2)—N(1)	1.94(2)	N(3)—C(12)	1.41(4)
Ga(3)—N(2)	1.96(2)	N(4)—C(9)	1.37(3)
Ga(3)—N(3)	2.02(2)	N(4)—C(13)	1.33(3)
Ga(1)—C(15)	1.92(3)	C(1)—C(4)	1.17(8)
Ga(2)—C(1)	1.90(4)	C(2)—C(6)	1.41(5)
Ga(3)—C(2)	1.89(3)	C(3)—C(5)	1.18(6)
Ga(3)—C(3)	1.89(3)	C(7)—C(13)	1.26(4)
N(1)—C(8)	1.34(3)	C(8)—C(10)	1.43(3)
N(1)—C(14)	1.44(3)	C(9)—C(11)	1.48(3)
N(2)—C(7)	1.38(3)	C(12)—C(14)	1.29(4)
N(2)—C(9)	1.32(4)	C(15)—C(16)	1.40(5)

(b) Valency angles			
N(4)—Ga(1)—N(4')	103(1)	C(2)—Ga(3)—C(3)	125(1)
N(4)—Ga(1)—C(15)	108(1)	Ga(2)—N(1)—C(8)	128(2)
N(4)—Ga(1)—C(15')	105(1)	Ga(2)—N(1)—C(14)	127(2)
C(15)—Ga(1)—C(15')	124(2)	C(8)—N(1)—C(14)	104(2)
N(1)—Ga(2)—N(1')	101(1)	Ga(3)—N(2)—C(7)	127(2)
N(1)—Ga(2)—C(1)	109(1)	Ga(3)—N(2)—C(9)	128(2)
N(1)—Ga(2)—C(1')	106(1)	C(7)—N(2)—C(9)	104(2)
C(1)—Ga(2)—C(1')	124(3)	Ga(3)—N(3)—C(8)	132(2)
N(2)—Ga(3)—N(3)	100.7(8)	Ga(3)—N(3)—C(12)	118(2)
N(2)—Ga(3)—C(2)	108(1)	C(8)—N(3)—C(12)	110(2)
N(2)—Ga(3)—C(3)	106(1)	Ga(1)—N(4)—C(9)	130(2)
N(3)—Ga(3)—C(2)	107(1)	Ga(1)—N(4)—C(13)	126(2)
N(3)—Ga(3)—C(3)	109(1)	C(9)—N(4)—C(13)	103(2)
Ga(2)—C(1)—C(4)	131(5)	N(2)—C(9)—N(4)	111(2)
Ga(3)—C(2)—C(6)	114(2)	N(2)—C(9)—C(11)	127(2)
Ga(3)—C(3)—C(5)	126(3)	N(4)—C(9)—C(11)	122(2)
N(2)—C(7)—C(13)	109(2)	N(3)—C(12)—C(14)	105(2)
N(1)—C(8)—N(3)	109(2)	N(4)—C(13)—C(7)	112(2)
N(1)—C(8)—C(10)	129(2)	N(1)—C(14)—C(12)	111(2)
N(3)—C(8)—C(10)	122(2)	Ga(1)—C(15)—C(16)	113(2)

been noted previously,^{21,22} the expansion and contraction of the usual tetrahedral angle of 109.5° expected about

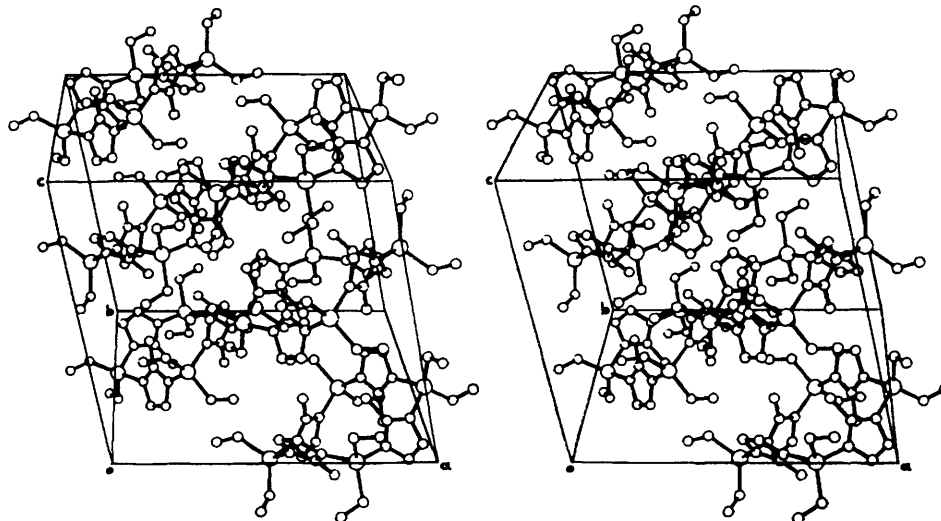


FIGURE 2 Stereoscopic view of the unit cell as viewed down *b*

the gallium atoms being due to steric requirements of the ligands. The geometry of the ethyl groups is rather ill-defined, with Ga—C—C angles 113—131°. The valency angles within the imidazolyl rings also have a wide range, but the large standard deviations in all C—C and N—C bond lengths and valency angles render invalid any detailed discussion of possible implications. Table 6 contains individual bond lengths and valency angles.

Figure 2 is a stereoscopic view of the unit cell viewed down *b*. There are no 'short' intermolecular non-bonded contacts <3.5 Å, but a number of intramolecular contacts in the range 3.0—3.5 Å are listed in Table 7. The overall 'square' nature of the molecule is reflected in angles: Ga(3')—Ga(2)—Ga(3) 89.62(7), Ga(1)—Ga(3)—Ga(2)

TABLE 7

Intramolecular non-bonded distances (Å), with estimated standard deviations in parentheses

C(4) ··· N(1)	3.48(6)	C(2) ··· C(3)	3.34(4)
C(1) ··· N(1')	3.06(4)	C(3) ··· N(2)	3.06(4)
C(1) ··· N(1)	3.13(4)	C(3) ··· N(3)	3.18(3)
C(1) ··· C(14')	3.42(5)	C(3) ··· C(7)	3.39(5)
C(1) ··· C(1')	3.35(8)	C(15) ··· N(4')	3.11(4)
C(2) ··· N(2)	3.12(3)	C(15) ··· N(4)	3.17(3)
C(2) ··· N(3)	3.14(4)	C(15) ··· C(13')	3.39(4)
C(2) ··· C(12)	3.31(5)	C(15) ··· C(15')	3.41(5)

90.36(5), and Ga(3')—Ga(1)—Ga(3) 89.65(6)°, and non-bonded distances: Ga(1) ··· Ga(3) 6.003(4), Ga(2) ··· Ga(3) 6.004(4), Ga(3) ··· Ga(3') 8.463(3), and Ga(1) ··· Ga(2) 8.517(6) Å. The shortest intramolecular non-bonded contacts all involve carbon atoms of the ethyl groups with nitrogen atoms of the imidazolyl rings, whilst the closest approach of the 2-methyl groups of the five-membered rings is 4.27(3) Å between C(10) and C(10') (*vide supra*).

EXPERIMENTAL

Materials were handled in a conventional high-vacuum line or in a glove box under oxygen-free dry nitrogen. Xylene was dried by heating under reflux over molten sodium metal for several days, followed by distillation.

Starting Materials.—Imidazole and 2-methylimidazole

(K and K laboratories) were used as purchased. Trimethylaluminum (Texas Alkyls) and trimethylboron (K and K laboratories) were vacuum distilled. Trimethylgallium,¹¹ triethylgallium,²³ and trimethylindium¹¹ were prepared as described previously.

Preparations.—*Tetrakis-μ-(2-methylimidazolyl)-tetrakis-(dimethylboron)*. Xylene (ca. 50 ml) and 2-methylimidazole

²³ A. W. Laubengayer and W. F. Gilliam, *J. Amer. Chem. Soc.*, 1941, **63**, 477.

(1.341 g, 16.4 mmol) were placed in a 500 ml break-seal bulb, which was cooled to -196°C and evacuated. Boron trimethyl (366 ml; 16.6 mmol) was condensed into the bulb, which was then flame-sealed. The bulb and contents were allowed to warm to room temperature and were then placed in an oven at 135°C for 3 days. The methane evolved was then measured (360 ml, 16.3 mmol). Crystals of the product were deposited on cooling.

Tetrakis- μ -(2-methylimidazolyl)-tetrakis(dimethylaluminum).—Aluminium trimethyl (0.5833 g, 8.1 mmol) and 2-methylimidazole (0.6610 g, 8.12 mmol) were heated under reflux in xylene under nitrogen for 24 h. The flask and its contents were cooled and crystals of the air-sensitive product were deposited.

The air-stable $[\text{Me}_2\text{Ga}(\text{N}_2\text{C}_4\text{H}_5)]_4$, $[\text{Et}_2\text{Ga}(\text{N}_2\text{C}_4\text{H}_5)]_4$, and $[\text{Me}_2\text{In}(\text{N}_2\text{C}_4\text{H}_5)]_4$ compounds were prepared similarly. Crystals of $[\text{Et}_2\text{Ga}(\text{N}_2\text{C}_4\text{H}_5)]_4$ suitable for X-ray analysis were obtained by recrystallization from xylene.

catena- μ -Imidazolyl-dimethylgallium.—Gallium trimethyl (1.7836 g, 15.5 mmol) and imidazole (1.052 g, 15.5 mmol) were heated under reflux for 5 h in xylene, after which the i.r. spectrum of the solution showed no $\nu(\text{NH})$. A white solid, $[\text{Me}_2\text{Ga}(\text{N}_2\text{C}_3\text{H}_3)]_x$, was deposited from the solution which did not redissolve on warming the flask plus contents.

Crystal Data.— $\text{C}_{32}\text{H}_{60}\text{Ga}_4\text{N}_8$, $M = 835.8$, Monoclinic, $a = 15.31(2)$, $b = 19.39(3)$, $c = 14.21(2)$ Å, $\beta = 101.30(9)^{\circ}$, $U = 4138$ Å³, $D_m = 1.32$, $Z = 4$, $D_c = 1.342$, $F(000) = 1728$. Mo- K_{α} radiation, $\lambda = 0.7107$ Å; $\mu(\text{Mo-}K_{\alpha}) = 27.5$ cm⁻¹. Space group $I2/a$ [non-standard setting of $C2/c$, (C_{2h}^2 , No. 15)] from intensity statistics and Patterson function.

Initially considerable difficulty was encountered in obtaining crystals suitable for X-ray analysis, since one batch was largely twinned, and another consisted of hollow crystals with trapped solvent. However, a third batch which had been left to crystallize for some weeks contained some colourless parallelepipeds elongated along c . Oscillation, Weissenberg, and precession photographs indicated monoclinic symmetry with the following systematic absences: hkl when $h + k + l = 2n + 1$, $h0l$ when $h = 2n + 1$; thus a choice arose between the space groups $I2/a$ and Ia [non-standard settings of $C2/c$ (C_{2h}^2 , No. 15) and Cc (C_2^2 , No. 9)]. A crystal of dimensions $ca. 0.5 \times 0.3 \times 0.7$ mm was used for intensity measurements and accurate unit-cell parameters were obtained by a least-squares fit of $17 \sin^2\theta(hkl)$ values measured on a General Electric XRD 6 diffractometer.

Intensity data were measured on a Datex-automated General Electric XRD 6 diffractometer by the $\theta-2\theta$ scan method at a rate of $2^{\circ} \text{min}^{-1}$ in 2θ . A scintillation counter equipped with a zirconium filter and pulse-height analyser ensured approximately monochromatic radiation. The crystal was mounted with c^* parallel to the goniostat axis. A total of 2 716 independent reflexions was measured with $2\theta \leq 45^{\circ}$ of which 1 182 were considered observed, having $I \geq \sigma(I)$ where $\sigma^2(I) = S + B + (0.08S)^2$, and S is scan count and B background. A standard reflexion was monitored periodically throughout data collection and used to scale the data. After scaling, Lorentz and polarization corrections were applied and structure amplitudes derived. No absorption corrections were made.

Data were placed on an absolute scale by Wilson's method,²⁴ and the resulting overall isotropic temperature

²⁴ A. J. C. Wilson, *Nature*, 1942, **150**, 151.

²⁵ I. L. Karle, K. S. Dragonette, and S. A. Brenner, *Acta Cryst.*, 1965, **19**, 713.

TABLE 8

Intensity statistics

	Found	Calc.	
		Centrosymmetric	Non-centrosymmetric
Mean $ E $	0.7501	0.7980	0.8860
Mean $ E ^2$	1.0355	1.0000	1.0000
Mean $ E^2 - 1 $	1.0893	0.9680	0.7360
% Reflexions with:			
$E > 3.0$	0.55	0.30	0.01
$E > 2.0$	5.89	5.00	1.80
$E > 1.0$	30.60	32.00	37.00

TABLE 9

Final positional (fractional $\times 10^4$) parameters,* with estimated standard deviations in parentheses

	x/a	y/b	z/c
Ga(1)	7 500	75(2)	0
Ga(2)	7 500	4 467(2)	0
Ga(3)	10 207(2)	2 270(2)	1 399(2)
N(1)	8 309(13)	3 831(10)	790(12)
N(2)	9 523(14)	1 532(10)	652(12)
N(3)	9 276(13)	3 025(11)	1 268(19)
N(4)	8 534(11)	710(12)	150(15)
C(1)	8 116(28)	4 928(26)	-851(27)
C(2)	10 450(19)	2 006(18)	2 704(19)
C(3)	11 081(19)	2 530(23)	698(22)
C(4)	8 873(41)	5 034(40)	-803(52)
C(5)	11 820(33)	2 690(33)	1 022(33)
C(6)	10 815(26)	1 342(22)	2 876(21)
C(7)	9 752(16)	1 165(17)	-90(17)
C(8)	8 762(17)	3 302(15)	508(18)
C(9)	8 766(19)	1 251(15)	769(14)
C(10)	8 754(15)	3 057(11)	-441(12)
C(11)	8 225(14)	1 450(11)	1 486(14)
C(12)	9 173(20)	3 376(17)	2 107(16)
C(13)	9 171(20)	706(14)	-364(17)
C(14)	8 585(21)	3 843(16)	1 815(20)
C(15)	7 534(20)	-387(14)	1 204(18)
C(16)	8 309(27)	-776(17)	1 498(19)
H(1A)	8 018	4 713	-1 526
H(1B)	7 825	5 442	-1 027
H(2A)	10 971	2 335	3 099
H(2B)	9 943	2 085	3 042
H(3A)	11 289	2 119	315
H(3B)	10 853	2 889	158
H(15A)	7 493	-36	1 742
H(15B)	7 019	-715	1 181
H(14)	8 277	4 212	2 242
H(12)	9 510	3 300	2 790
H(13)	9 181	349	-937
H(7)	10 289	1 250	-383
H(10A)	9 030	3 422	-814
H(10B)	9 087	2 615	-476
H(10C)	8 118	2 984	-817
H(11A)	8 213	1 996	1 561
H(11B)	7 551	1 334	1 297
H(11C)	8 433	1 274	2 151
H(4A)	9 264	4 691	-241
H(4B)	9 259	5 124	-1 228
H(4C)	9 094	5 523	-267
H(16A)	8 861	-547	1 276
H(16B)	8 536	-805	2 247
H(16C)	8 292	-1 261	1 264
H(6A)	11 080	1 196	2 294
H(6B)	11 207	1 245	3 461
H(6C)	10 253	1 004	2 818
H(5A)	11 998	2 598	1 791
H(5B)	12 365	2 709	798
H(5C)	11 792	3 317	1 191

* Hydrogen atoms bear the numbers of the carbon atom to which they are bonded.

factor of 8.7 \AA^2 indicated the presence of quite large thermal motion in the crystal, a fact already apparent from the absence of 'observed' high-angle reflexions ($> 30^{\circ}$ in 2θ) in

some of the preliminary photographs and in the intensity data itself. Intensity statistics²⁵ suggested $I2/a$ to be the most likely choice of space group (Table 8) and so a solution was attempted in that space group. With four molecules per unit cell in $I2/a$, each molecule must possess a centre of symmetry or two-fold rotation symmetry. Two-fold symmetry was initially assumed, the two-fold axis passing either (a) through two of the non-adjacent gallium atoms, or (b) perpendicularly through the centre of the plane containing the four gallium atoms. Any other choices would have to accommodate disorder. The vector distribution in a three-dimensional sharpened Patterson function indicated choice (a), with two gallium atoms on the two-fold axis and one in a general position. A structure-factor calculation based on the three gallium atoms gave R 0.32. The remainder of the non-hydrogen atoms were located in successive difference-Fourier syntheses. Refinement was by full-matrix least-squares methods in which the function minimized was $\Sigma w(F_o - F_c)^2$ with weights derived from counting statistics. All non-hydrogen atoms were refined with anisotropic thermal parameters and at convergence R was 0.115. Inclusion of all hydrogen atoms in calculated positions (C-H 1.0 Å) with U_{iso} 0.12 Å² gave R 0.105. Four low-angle reflexions ($-2, -2, 8$; $-1, -1, 4$; $-1, -1, 2$; and $2, 2, 0$) were then given zero weight in the refinement because of suspected extinction effects, and two cycles of refinement brought convergence to R 0.101 and R' [defined as $\Sigma w(F_o - F_c)^2 / \Sigma w F_o^2$] 0.100. The mean and largest shift-to-error ratios in the refined parameters were 0.09 and 0.38. The weighting scheme chosen (absolute weights) gave constant values of $w(F_o - F_c)^2$ over all ranges of F_o , and the value obtained for the error in an observation of unit weight was 1.14. The relatively high final value of R is assumed to be due to the paucity of data at the $3\sigma(I)$ level, *i.e.* the fact that data down to the $\sigma(I)$ level had to be used in order to have sufficient data for refinement. A final difference-Fourier synthesis revealed maximum fluctuations in the residual electron density of $\pm 0.7 \text{ e}\text{\AA}^{-3}$. Scattering factors for gallium, nitrogen, and carbon were taken from ref. 26 and those for hydrogen from ref. 27. Those for gallium were

* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

²⁶ D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

corrected for the real and imaginary parts of anomalous dispersion.²⁸ Measured and calculated structure amplitudes are listed in Supplementary Publication No. SUP 21333 (26 pp., 1 microfiche).^{*} Final positional and thermal parameters are given in Tables 9 and 10.

TABLE 10

Final thermal parameters * ($U_{ij} \times 10^3$ for Ga, $\times 10^2$ for other atoms), with estimated standard deviations in parentheses

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ga(1)	157(4)	100(4)	93(3)	0	45(2)	0
Ga(2)	168(4)	115(4)	119(3)	0	42(3)	0
Ga(3)	95(2)	181(3)	83(2)	-12(2)	21(1)	9(2)
N(1)	15(2)	11(2)	7(1)	-1(1)	5(1)	-1(1)
N(2)	11(2)	16(2)	8(1)	2(2)	4(1)	2(1)
N(3)	9(2)	15(2)	14(2)	-0(1)	4(1)	-3(2)
N(4)	8(1)	19(2)	8(1)	2(1)	3(1)	4(1)
C(1)	24(5)	22(4)	14(3)	-2(4)	2(3)	7(2)
C(2)	13(2)	22(4)	10(2)	2(2)	2(2)	2(2)
C(3)	11(2)	33(5)	14(2)	-1(3)	5(2)	-2(2)
C(4)	37(9)	36(7)	41(8)	-7(8)	15(7)	14(5)
C(5)	29(5)	54(8)	23(5)	-15(7)	16(4)	-4(5)
C(6)	24(4)	29(5)	10(2)	2(4)	3(2)	3(3)
C(7)	9(2)	16(3)	8(2)	1(2)	4(1)	1(2)
C(8)	10(2)	14(3)	8(2)	1(2)	0(1)	1(2)
C(9)	12(2)	14(3)	3(1)	3(2)	1(1)	1(1)
C(10)	18(2)	12(2)	5(1)	4(2)	2(1)	-1(1)
C(11)	13(2)	12(2)	10(1)	-1(1)	6(1)	-3(1)
C(12)	15(3)	17(3)	6(2)	2(2)	2(2)	-4(2)
C(13)	11(3)	12(2)	12(2)	2(2)	6(2)	-0(2)
C(14)	17(3)	15(3)	9(2)	-0(2)	5(2)	-4(2)
C(15)	19(3)	9(2)	15(2)	1(2)	6(2)	-0(2)
C(16)	31(5)	18(3)	13(2)	7(3)	10(3)	4(2)

* In the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

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²⁷ R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

²⁸ D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.