The Crystal and Molecular Structure of a Dideuterio(pyrazol-1-yl)gallane Dimer [1]

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Crystals of the title compound are orthorhombic, $a = 11{\cdot}518(2)$, $b = 11{\cdot}278(1)$, $c = 8{\cdot}267(1)$ Å, space group $Cmc2_1$, $Z = 4$ (dimeric units). The structure was determined from diffractometer data by Patterson and Fourier syntheses, and refined by full-matrix least-squares methods to R 0·049 for 491 observed reflexions. The molecule is V-shaped, the angle between the unique portion of the molecule and its crystallographic mirror image being 128·4°, and the six-membered Ga(N–N)$_2$Ga ring being in the boat conformation. Mean dimensions are: Ga–N 1·974, N–N 1·34, N–C 1·35, C–C 1·35 Å; N–Ga–N′ 96·6, Ga–N–N 123·6°.

As part of a continuing investigation [2] of the reactions of Group III compounds with ligands containing active hydrogen, pyrazolyl $[C_3H_3N_2]^{\bullet}$ derivatives have been prepared containing aluminium and gallium moieties. Our results present the first structural characterization of a member of the symmetrical dimeric class of compounds, $[C_3H_3N_2{\cdot}MR_2]_2$ (where M = B, Al, or Ga; R = H, D, Me, or Et). Crystal structures of a number of related poly-(pyrazol-1-yl)borate transition-metal complexes have been reported previously,[3-7] and have in common unsymmetrical six-membered rings, B(N–N)$_2$M′ (where M′ = Mo or Co), in pseudo-boat conformations.

EXPERIMENTAL

The present gallane compound was prepared by reaction of equimolar amounts of pyrazole and (trimethylamine)-trideuteriogallane in benzene solution. Stoicheiometric amounts of trimethylamine and hydrogen deuteride were liberated and the gallane product $[C_3H_3N_2{\cdot}GaD_2]_2$, isolated as a volatile solid [Found: Ga, 49·0; D (hydrol.), 2·8%; M, 283,285 (C_6H_6 soln.). $C_6H_6D_4N_4Ga_2$ requires Ga, 49·5; D (hydrol.) 2·8%; M, 281·4].

Crystal Data.—$C_6H_6D_4N_4Ga_2$, $M = 281{\cdot}4$, Orthorhombic, $a = 11{\cdot}518(2)$, $b = 11{\cdot}278(1)$, $c = 8{\cdot}267(1)$ Å, $U = 1073{\cdot}9$ Å^3, D_m not measured because of crystal instability, $Z = 4$, $D_c = 1{\cdot}740$, $F(000) = 544$. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) = 63·3 cm^{-1}. Space group $Cmc2_1$ (C^{12}_{2v}, No. 36) from intensity statistics, and Patterson function.

Oscillation, Weissenberg, and precession photographs indicated orthorhombic symmetry with the following systematic absences: hkl when $h + k = 2n + 1$, $h0l$ when $l = 2n + 1$; thus a choice arose between the space groups $Cmc2_1$ (C^{12}_{2v}, No. 36), $Cmcm$ (D^{17}_{2h}, No. 63), and $C2cm$ [nonstandard setting of $Ama2$, (C^{16}_{2v}, No. 40)]. A cylindrically shaped crystal of dimensions *ca.* 0·8 × 0·2 mm in diameter was sealed in a capillary tube under nitrogen for intensity measurements. Intensity data were measured on a Datex-automated General Electric XRD 6 diffractometer by use of the θ—2θ scan method at a rate of 2° min^{-1} in 2θ. A scintillation counter equipped with a nickel filter and pulse-height analyser ensured approximately monochromatic radiation. 545 Independent reflexions were measured ($2\theta \leqslant 135°$ for Cu radiation, giving a minimum interplanar distance of 0·83 Å) of which 491 had intensities $>3\sigma(I)$ [where $\sigma(I)$ is defined by $\sigma^2(I) = S + B + (0{\cdot}05S)^2$, and S is scan count and B background] and were classified as observed. A standard reflexion was monitored every forty reflexions and its intensity fluctuated by up to 10% throughout the data collection. Data were accordingly scaled, Lorentz and polarization corrections applied, and the structure amplitudes derived. No absorption corrections were applied.

Intensity statistics [8] strongly indicated a non-centrosymmetric space group (see Table 1) and so the centrosymmetric space group $Cmcm$ was initially ruled out. From the vector distribution in the three-dimensional Patterson function, the structure could only be interpreted successfully in terms of the space group $Cmc2_1$. Since $Cmc2_1$ is a polar space group and the z co-ordinate in-

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[1] Preliminary communication, D. F. Rendle, A. Storr, and J. Trotter, *J.C.S. Chem. Comm.*, 1973, 189.

[2] A. Storr, B. S. Thomas, and A. D. Penland, *J.C.S. Dalton*, 1972, 326.

[3] L. J. Guggenberger, C. T. Prewitt, P. Meakin, S. Trofimenko, and J. P. Jesson, *Inorg. Chem.*, 1973, **12**, 508.

[4] M. R. Churchill, K. Gold, and C. E. Maw, jun., *Inorg. Chem.*, 1970, **9**, 1597.

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[7] J. L. Calderon, F. A. Cotton, and A. Shaver, *J. Organometallic Chem.*, 1972, **37**, 127.

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

determinate, the origin was fixed by assigning a z co-ordinate of 0·0 to one of the gallium atoms. Both heavy-atom positions were determined from the Patterson function and a structure-factor calculation gave R 0·243. A three-dimensional Fourier synthesis phased on the heavy atoms revealed the remainder of the structure. Refinement was by full-matrix least-squares methods with anisotropic temperature factors for all non-hydrogen and deuterium atoms. Hydrogen and deuterium atoms were included in the structure-factor calculations with fixed positional parameters (assuming C–D 1·08 and Ga–D 1·56 Å with appropriate sp^2 geometry about the carbon atoms, and sp^3 geometry about the gallium atoms) and thermal parameters (U_{iso} 0·063 Å^2).

TABLE 1

Intensity statistics

		Calc.	
	Found	Centrosymmetric	Non-centrosymmetric
Mean $\|E\|$	0·8809	0·7980	0·8860
Mean $\|E\|^2$	0·9841	1·0000	1·0000
Mean $\|E^2 - 1\|$	0·7067	0·9680	0·7360
% Reflexions with:			
$E > 3·0$	0·0	0·30	0·01
$E > 2·0$	0·55	5·00	1·80
$E > 1·0$	40·18	32·00	37·00

Scattering factors[9] for gallium, nitrogen, and carbon were corrected for the real and imaginary parts of anomalous dispersion. The function minimized was $\Sigma w(F_o - F_c)^2$, with weights w derived from counting statistics. Refinement converged with R at 0·050 and R' [defined as $\Sigma w(F_o - F_c)^2/\Sigma wF_o^2$] at 0·061. Preliminary data and results at this time were published previously[1] but further work has established the correct 'orientation' of the unit-cell axes (the term 'absolute configuration' is inappropriate here since the molecule possesses a mirror plane). The co-ordinates of the Ga, N, C, H, and D atoms at R 0·050 were replaced with co-ordinates of the opposite sign and then these parameters were refined to convergence giving R 0·049 and R' 0·60; this decrease, according to Hamilton's test,[10] is significant at a confidence level $>$99·5%. As a result of this refinement the two independent Ga–N distances now differ by only 1σ whereas they had differed by $>2\sigma$ at the conclusion of the R 0·050 refinement. At convergence the maximum shift to error ratio in the refined parameters was 0·18. A final difference-Fourier synthesis was featureless except for one peak of height *ca.* 2e Å^{-3} in the region of one of the gallium atoms, and so the structural analysis was assumed to be complete and correct. Measured and calculated structure factors are listed in Supplementary Publication No. SUP 20777 (6 pp., 1 microfiche).*

Final positional and thermal parameters of the molecule refined with axes of the correct 'orientation' are given in Tables 2 and 3. Atoms are in positions 4(*a*) and 8(*b*), the molecule possessing a crystallographic mirror plane which contains two gallium atoms and four deuterium atoms. Bond lengths and valency angles are listed in Table 4.

TABLE 2

Final positional (fractional × 10^4) parameters, with estimated standard deviations in parentheses

	x	y	z
Ga(1)	0	−0653(1)	0
Ga(2)	0	−3245(1)	−2393(3)
N(1)	1281(6)	−1104(6)	−1468(10)
N(2)	1288(6)	−2095(5)	−2366(11)
C(1)	2268(9)	−0518(8)	−1777(16)
C(2)	2931(9)	−1152(10)	−2839(17)
C(3)	2305(10)	−2120(9)	−3186(15)
H(1)	2472	0290	−1332
H(2)	3728	−0919	−3287
H(3)	2545	−2794	−3998
D(1)	0	−1413	1578
D(2)	0	0689	0449
D(3)	0	−4051	−3923
D(4)	0	−4036	−0841

TABLE 3

Final thermal parameters * (components of the vibration tensors, U in Å^2 × 10^2) with standard deviations in parentheses

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ga(1)	6·85(9)	8·64(11)	5·93(8)	0	0	−1·20(8)
Ga(2)	7·05(9)	5·23(7)	9·99(14)	0	0	−0·42(9)
N(1)	5·51(34)	7·37(41)	6·43(43)	−0·09(34)	0·44(32)	−0·19(37)
N(2)	5·65(33)	5·85(32)	7·80(45)	0·11(26)	0·73(40)	0·43(47)
C(1)	8·03(64)	8·55(61)	8·26(64)	−2·33(54)	−0·02(60)	−0·82(54)
C(2)	7·12(57)	10·81(84)	10·39(90)	−1·47(58)	2·58(63)	0·48(76)
C(3)	7·04(57)	8·18(62)	9·00(69)	1·01(54)	1·96(59)	0·27(56)

* The temperature factor expression is of the type: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$

TABLE 4

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

(*a*) Bond distances

Ga(1)–N(1)	1·977(8)	N(2)–C(3)	1·353(12)
Ga(2)–N(2)	1·971(6)	C(1)–C(2)	1·365(15)
N(1)–N(2)	1·342(10)	C(2)–C(3)	1·340(15)
N(1)–C(1)	1·339(11)		

(*b*) Valency angles

N(1′)–Ga(1)–N(1)	96·5(0·5)	Ga(2)–N(2)–C(3)	129·2(0·7)
N(2′)–Ga(2)–N(2)	97·7(0·4)	C(3)–N(2)–N(1)	107·4(0·7)
Ga(1)–N(1)–N(2)	123·9(0·5)	N(1)–C(1)–C(2)	109·8(0·9)
Ga(1)–N(1)–C(1)	128·6(0·7)	C(1)–C(2)–C(3)	105·3(1·0)
C(1)–N(1)–N(2)	107·5(0·8)	N(2)–C(3)–C(2)	110·0(0·9)
Ga(2)–N(2)–N(1)	123·4(0·6)		

DISCUSSION

Figure 1 is a general view of the molecule, showing the symmetrical six-membered Ga(N–N)$_2$Ga ring in the boat conformation. Primed and unprimed atoms are related by the crystallographic mirror plane. Best planes through one pyrazolyl ring C(1)—(3), N(1), and N(2) and the group of atoms Ga(1), N(1), N(2), and Ga(2) show that both sets of atoms are planar, the dihedral angle of 1·2° between the two planes showing that they are almost coplanar. This small deviation

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. are sent as full-size copies.)

[9] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[10] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.

from coplanarity would certainly not hinder delocalization of 6π electrons in each C_3N_2 moiety which presumably gives an added stability to the boat conformation. The deviation from a totally planar configuration for the whole tricyclic molecule, an arrangement which would also allow delocalization of the π electrons but one which is somewhat more strained, is indicated by the angle between the plane formed by Ga(1), Ga(2), N(1), N(2), C(1)—(3) and its corresponding mirror image. A planar arrangement would give this angle as 180°; the observed angle is 128·4°. The gallium atoms in fact lie 0·73 [Ga(1)], and 0·70 Å [Ga(2)], above the plane containing the four nitrogen atoms. Table 5 lists important least-squares planes and dihedral angles within the molecule.

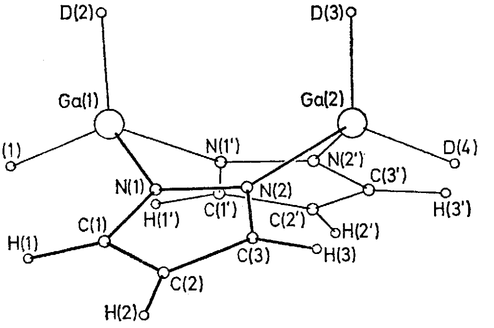

FIGURE 1 Molecular structure

TABLE 5

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

Plane (1): N(1), N(2), C(1)—(3)

$$0{\cdot}4359X + 0{\cdot}4871Y - 0{\cdot}7568Z = -0{\cdot}3235$$

[Ga(1) − 0·035(1), Ga(2) 0·038(2), N(1) − 0·007(8), N(2) 0·006(8), C(1) 0·012(12), C(2) − 0·005(12), C(3) − 0·006(12)]

Plane (2): Ga(1), Ga(2), N(1), N(2), C(1)—(3)

$$0{\cdot}4355X + 0{\cdot}5043Y - 0{\cdot}7456Z = -0{\cdot}3714$$

[Ga(1) − 0·0002(8), Ga(2) 0·0007(22), N(1) 0·006(8), N(2) − 0·008(8), C(1) 0·035(12), C(2) − 0·004(13), C(3) − 0·027(11)]

Plane (3): Ga(1), Ga(2), N(1′), N(2′), C(1′)—(3′)

$$-0{\cdot}4355X + 0{\cdot}5043Y - 0{\cdot}7456Z = -0{\cdot}3714$$

[Ga(1) − 0·0002(8), Ga(2) 0·0007(22), N(1′) 0·006(8), N(2′) − 0·008(8), C(1′) 0·035(12), C(2′) − 0·004(13), C(3′) − 0·027(11)]

Plane (4): N(1), N(2), N(1′), N(2′)

$$0{\cdot}5528Y - 0{\cdot}8333Z = 0{\cdot}3235$$

[Ga(1) − 0·731(1), Ga(2) − 0·700(3), N(1) 0, N(2) 0, N(1′) 0, N(2′) 0)]

Plane (5): Ga(1), N(1), N(1′)

$$0{\cdot}9225Y - 0{\cdot}3861Z = -0{\cdot}6796$$

Plane (6): Ga(2), N(2), N(2′)

$$0{\cdot}0173Y - 0{\cdot}9999Z = 1{\cdot}9146$$

Plane (7): Ga(1), Ga(2), N(1), N(2)

$$0{\cdot}4347X + 0{\cdot}5047Y - 0{\cdot}7459Z = -0{\cdot}3718$$

[Ga(1) − 0·0000(8), Ga(2) 0·0002(22), N(1) 0·008(8), N(2) − 0·007(8)]

(*b*) Dihedral angles (°) between planes

(1)–(2)	1·2	(4)–(5)	146·3
(1)–(4)	154·1	(4)–(6)	147·4
(1)–(7)	1·2	(5)–(6)	113·7
(2)–(3)	128·4		

The mean Ga–N distance [1·974(5) Å] agrees well with the corresponding distances [1·97(9) and 1·97(2) Å] in previously documented gallane compounds, Me_3NGaH_3 (ref. 11) and $[(CH_2)_2N{\cdot}GaH_2]_3$ (ref. 12) but is considerably shorter than Ga–N distances quoted in $[GaCl_2(bipy)_2]^+[GaCl_4]^-$ [2·103(6) Å],[13] $GaCl_3$,terpyridyl [2·113(6), 2·034(7) Å],[14] and GaH,edta,H_2O [2·097(6), 2·182(5) Å].[15] However, this is completely consistent with the fact that in the gallane compounds gallium is tetrahedrally co-ordinated whilst in the last three compounds it is octahedrally co-ordinated: an increase in bond length with co-ordination number. The N(1)–Ga(1)–N(1′) and N(2)–Ga(2)–N(2′) valency angles of 96·5 and 97·7°, while not significantly different from one another, are considerably different from the normal tetrahedral angles associated with a regular six-membered ring in the boat conformation. This may be due to the fact that the ring is heterocyclic (with some bonds much longer than others) and also to the trigonal planar geometry forced upon the nitrogen atoms by the nature of the pyrazolyl ligand.

TABLE 6

Selected intra- and inter-molecular non-bonded distances (Å)

(*a*) Intramolecular distances

Ga(1) · · · N(2)	2·945(8)	N(1) · · · N(1′)	2·951(15)
Ga(1) · · · C(1)	3·001(11)	N(2) · · · N(2′)	2·967(13)
Ga(1) · · · Ga(2)	3·529(2)	C(2) · · · C(2′)	6·75(2)
Ga(2) · · · N(1)	2·931(7)	N(1) · · · N(2′)	3·25(1)
Ga(2) · · · C(3)	3·014(11)		

(*b*) Intermolecular distances

Ga(1) · · · N(1^{I})	3·825(8)	N(2) · · · C(3^{II})	3·918(13)
Ga(1) · · · C(1^{I})	3·958(12)	C(1) · · · C(2^{III})	3·838(18)
N(1) · · · C(3^{II})	3·746(13)		

Roman numeral superscripts refer to the following equivalent positions:

I $-x, -y, \frac{1}{2} + z$
II $-\frac{1}{2} - x, -\frac{1}{2} - y, \frac{1}{2} + z$
III $x, -y, \frac{1}{2} + z$

The bond distances and valency angles within the pyrazolyl ring approximate to values recorded previously[3-7] for such a system, including pyrazole itself.[16] The distances (Table 4) compare well with the corresponding ones in, *e.g.*, bis[hydrotris(1-pyrazolyl)borato]-cobalt(II)[4] (N–N 1·364, C–N 1·307—1·358, and C–C

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[12] W. Harrison, A. Storr, and J. Trotter, *J.C.S. Dalton*, 1972, 1554.

[13] R. Restivo and G. J. Palenik, *Chem. Comm.*, 1969, 867.

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[15] C. H. L. Kennard, *Inorg. Chim. Acta*, 1967, **1**, 347.

[16] H. W. W. Ehrlich, *Acta Cryst.*, 1960, **13**, 946.

1·347—1·428 Å). The sum of the internal angles of the five-membered ring is 540°.

The Ga(1) · · · Ga(2) intramolecular non-bonded distance is 3·529(2) Å, while the distance between the carbon atoms at the extremities of the molecule [C(2) and C(2′)] is 6·75(2) Å. The packing of the molecules within the crystal lattice as viewed down *b* is shown in Figure 2. The molecules are separated by normal van der Waals distances, the closest approach being 3·746(13) Å between N(1) and C(3) of neighbouring molecules. Selected non-bonded intra- and intermolecular contacts are listed in Table 6.

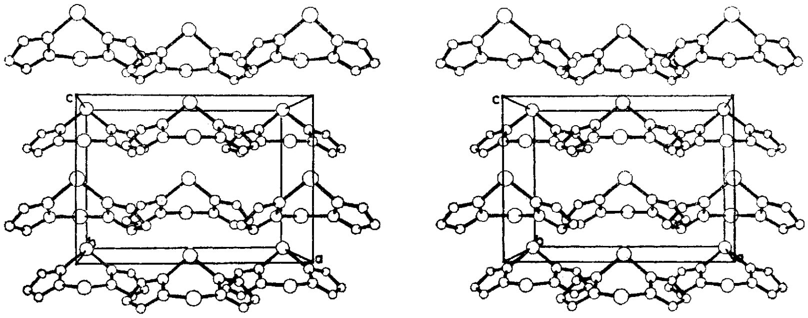

FIGURE 2 Stereoscopic view of the unit cell

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