Crystal Structure of Tetramethylammonium Hexachlorodigallate(II)

By **Kevin L. Brown** and **David Hall**,* Chemistry Department, University of Auckland, New Zealand

Crystals of $(Me_4N)_2Ga_2Cl_6$ are cubic, $a = 13{\cdot}097$ Å, space group $Pa3$, $Z = 4$. The structure was solved from diffractometer data by Patterson and Fourier methods and refined by least-squares techniques to R 0·076 for 384 observed reflections. The analysis confirms the existence of a $Ga_2Cl_6^{2-}$ ion, of symmetry D_{3d}, with a Ga–Ga bond of length 2·39 Å.

THE apparently divalent simple halides of gallium have proven[1] to be mixed valence compounds $Ga^+GaX_4^-$, but by contrast compounds which are believed to contain hexahalogenodigallate anions display an intense Raman band which does suggest the existence of a gallium–gallium bond,[2] and hence an anion in which gallium is formally divalent. The crystal structure of $(Me_4N)_2Ga_2Cl_6$ has been determined in order to confirm this deduction.

EXPERIMENTAL

Many of the crystals were perfect octahedra, but were invariably multiple. Single crystals could be obtained by crushing the octahedra, and a roughly equant fragment (min. and max. dimensions 0·030 and 0·037 cm respectively) was used for data collection.

Crystal Data.—$C_8H_{24}Ga_2Cl_6N_2$, $M = 500{\cdot}5$, Cubic, $a = 13{\cdot}097(4)$ Å, $U = 2246$ Å^3, D_m (by flotation) $= 1{\cdot}47$, $Z = 4$, $D_c = 1{\cdot}44$ g cm^{-3}. Systematic absences: $hk0$, when k odd, and cyclic equivalents indicate space group $Pa3$ (No. 205). Mo-K_α radiation, Zr-filtered, $\lambda = 0{\cdot}71069$ Å; μ(Mo-K_α) $= 31{\cdot}4$ cm^{-1}. The cell constant (and its error) were determined by the method of Busing and Levy.[3]

Intensities for all reflections with h, k, l all positive and $20 < 30°$ were scanned by use of a Hilger and Watts automated diffractometer, and a stationary background count taken at each end of the scan. A total of 913 data were considered observed, having $I > 2\sigma(I)$. A feature (also apparent on photographs) was the almost complete absence of observable reflections for which d was $<0{\cdot}8$ Å. No absorption corrections were applied, because of the difficulty in accurately describing the crystal fragment. For the equivalent reflections hkl, klh, lhk, the mean discrepancy between mean and individual values was 3·9%. The unique data set comprised 384 observed reflections.

Space-group considerations restrict the gallium atom to positions of type (x,x,x), and the parameter was obtained from a Patterson synthesis. Other atoms were located from subsequent difference-Fourier syntheses. Refinement by block-diagonal least-squares reduced R to 0·127, at which stage hydrogen atoms were located on a difference-Fourier synthesis. Subsequent refinement by full-matrix least-squares, assuming fixed isotropic thermal parameters (7·5 Å^2) for hydrogen atoms but refining their positional parameters, and refining anisotropic thermal parameters as well as positional parameters for all other atoms, gave a final R of 0·076.* Atom co-ordinates and thermal parameters are listed in Table 1. Bond lengths and angles are listed in Table 2, but in view of the very large observed

---

* Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20717 (2 pp., 1 microfiche). For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue (items less than 10 pp. are supplied as full size copies).

[1] G. Garton and H. M. Powell, *J. Inorg. Nuclear Chem.*, 1957, **4**, 84.

[2] C. A. Evans and M. J. Taylor, *Chem. Comm.*, 1969, 1201.

[3] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1967, **22**, 457.

thermal parameters, these may require correction. The errors quoted in Table 2 are solely the least-squares estimates. The various possible corrections to the observed bond lengths,[4] depending on the mode of thermal motion assumed, are also listed in Table 2. A view of the anion and adjacent cations is shown in Figure 1 and a projected view of the structure is shown in Figure 2.

TABLE 1

(*a*) Atom co-ordinates

Atom	x/a	y/b	z/c
Ga	0·05269(10)	0·05269(10)	0·05269(10)
Cl	0·0480(3)	0·2154(2)	0·0126(3)
N	0·2749(9)	0·02749(9)	0·2749(9)
C(1)	0·3347(15)	0·3347(15)	0·3347(15)
C(2)	0·2465(16)	0·1822(15)	0·3305(18)
H(1)	0·373(9)	0·319(9)	0·367(10)
H(2)	0·325(8)	0·144(8)	0·347(8)
H(3)	0·265(10)	0·143(9)	0·277(8)
H(4)	0·210(9)	0·198(9)	0·392(8)

(*b*) Thermal parameters ($\times 10^4$) *

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Ga	119(1)	119(1)	119(1)	−3·4(9)	−3·4(9)	−3·4(9)
Cl	167(4)	118(3)	161(3)	4(2)	4(2)	10(2)
N	112(5)	112(5)	112(5)	9(8)	9(8)	9(8)
C(1)	296(31)	296(31)	296(31)	−91(25)	−91(25)	−91(25)
C(2)	208(20)	172(19)	223(25)	29(14)	107(17)	41(15)

* The scattering factor for an atom is expressed as:

$$f = f_0 \exp - (b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl).$$

TABLE 2

(*a*) Bond lengths (Å)

Ga–Ga	2·390(2)	C(1)–H(1)	0·70(13)
Ga–Cl	2·196(4)	C(2)–H(2)	1·16(11)
N–C(1)	1·36(2)	C(2)–H(3)	0·91(12)
N–C(2)	1·46(2)	C(2)–H(4)	0·96(12)

(*b*) Bond angles (°)

Ga–Ga–Cl	113·9(1)	C(1)–N–C(2)	109·7(14)
Cl–Ga–Cl	104·6(1)	C(2)–N–C(2)	109·2(14)

(*c*) Corrections to bond lengths for thermal motion (Å)

Bond	Min. correction	Riding motion	Independent motion	Max. correction
Ga–Ga	0·000	0·000	0·043	0·087
Ga–Cl	0·002	0·014	0·053	0·154
N–C(1)	0·021	0·075	0·144	0·267
N–C(2)	0·011	0·049	0·114	0·216

DISCUSSION

The existence of the $Ga_2Cl_6^{2-}$ ion with direct Ga–Ga bond[2] is confirmed, the bond length being 2·390(2) Å, although the corrected value could be somewhat higher (Table 2). The only other reported value for directly bonded gallium atoms is 2·46 Å in the chain structure of GaS,[5] but no error is quoted for this. The covalent radius previously deduced[6] for gallium(I) is 1·22 Å. The $Ga_2Cl_6^{2-}$ ion has D_{3d} symmetry (by space-group requirement) with approximately tetrahedral geometry about the gallium, although the increased value of the Ga–Ga–Cl angle (113·9°) with regard to Cl–Ga–Cl (104·6°) is notable. The Ga–Cl bond length [2·196(4) Å] agrees well with those observed in Ga_2Cl_6 in the vapour phase[7] (2·22 Å) and in the $GaCl_4^-$ ion[1] (2·19 Å), suggesting that no great thermal motion correction is required and that the riding model ($\Delta = 0{\cdot}014$ Å) might be appropriate.

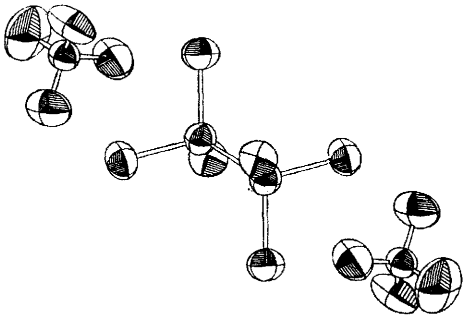

FIGURE 1 The anion and adjacent cations, showing thermal vibration ellipsoids

The space-group required symmetry of the tetramethylammonium cation is C_3. The bond angles about the nitrogen are within error of tetrahedral values, but the two independent N–C bond lengths are significantly different, the unique N–C(1) bond (1·35 Å) being very much shorter than the expected value of 1·48 Å. The discrepancies are well within the range of possible thermal motion correction however, particularly if one assumes that atom C(1) is vibrating independently

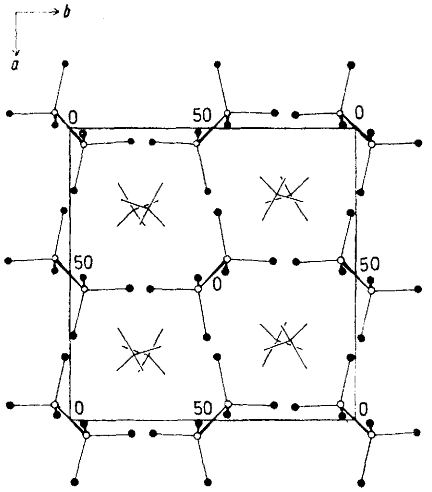

FIGURE 2 The structure projected on (001). Numbers represent the *z* co-ordinates of the centres of Ga–Ga bonds

---

[4] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1964, **17**, 142.

[5] H. Hahn and G. Frank, *Z. anorg. Chem.*, 1955, **278**, 333.

[6] F. M. Brewer, J. R. Chadwick, and G. Garton, *J. Inorg. Nuclear Chem.*, 1961, **23**, 45.

[7] D. P. Stevenson and V. Schomaker, *J. Amer. Chem. Soc.*, 1942, **64**, 2514.

from (or to some extent riding upon) the remainder of the ion, which is itself vibrating mainly as a unit.

The cations are situated along the crystallographic triad axis such that the three atoms C(2) are the near neighbours of the chlorines of the $Ga_2Cl_6^{2-}$ ion. The C(2) and Cl atoms are rotated by 25° from the perfectly staggered mutual orientation, but there are no approaches between them of $<3{\cdot}86$ Å.

We thank Dr. M. J. Taylor for suggesting this problem, supplying the crystals, and for his constant interest.

[2/2163 *Received, 18th September, 1972*]