JOHNSTON, D. C. (1977). *Solid State Commun.* **24**, 699–702.

JOHNSTON, D. C. & MACKAY, H. B. (1979). *Bull. Am. Phys. Soc.* **24**, 390.

KUZMA, JU. B. & BILONIZHKO, N. S. (1972). *Sov. Phys. Crystallogr.* **16**, 897–898.

KUZMA, JU. B. & BILONIZHKO, N. S. (1978). *Dopov. Akad. Nauk Ukr. RSR Ser. A*, **3**, 275–277.

MAPLE, M. B. (1981). *Proc. International Conference on Ternary Superconductors*, edited by G. SHENOY. New York: North-Holland.

ROGL. P. (1979). *Monatsh. Chem.* **110**, 235–243.

ROGL. P. (1980). *Monatsh. Chem.* **111**, 517–527.

STEWART, J. M. (1976). The XRAY 76 system. Tech. Rep. TR446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

VANDENBERG, J. M. & MATTHIAS, B. T. (1977). *Proc. Natl Acad. Sci. USA*, **74**, 1336–1337.

YVON, K. (1981). *Superconductivity in Ternary Compounds*, Vol. I, edited by B. MAPLE & Ø. FISCHER, Ch. 2. Berlin: Springer Verlag.

YVON, K. & GRÜTTNER, A. (1980). *Superconducitivity in d- and f-Band Metals*, edited by H. SUHL & B. MAPLE, pp. 515–519. New York: Academic Press.

Structure of Bis[dibromo(1,4-dioxane)gallium]

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Abstract. $[Ga_2Br_4(C_4H_8O_2)_2]$, $C_8H_{16}Br_4Ga_2O_4$, triclinic $P\bar{1}$, $a = 9\cdot039$ (5), $b = 11\cdot24$ (5), $c = 9\cdot018$ (5) Å, $\alpha = 106\cdot75$ (2), $\beta = 72\cdot34$ (2), $\gamma = 97\cdot52$ (2)°, $Z = 2$, $D_x = 2\cdot527$, $D_m = 2\cdot51$ Mg m⁻³. The structure has been solved from 1195 diffractometer-measured intensities and refined by full-matrix least squares to $R = 0\cdot0827$. The complex contains a Ga—Ga bond and is similar to the chloride complex.

Introduction. Although the metal—metal-bonded form of Ga_2Cl_4 is not known, stable complexes of the halide may be prepared, *e.g.* $Ga_2Cl_4.2(dioxane)$ (Beamish, Small & Worrall, 1979), $Ga_2Cl_6^{2-}$ (Brown & Hall, 1973), which contain Ga—Ga bonds. The Raman spectra of these two complexes contain very strong bands in similar positions (Beamish *et al.*, 1979) and it has been suggested that the presence of such intense bands may be used to identify Ga—Ga bonds (Tan & Taylor, 1974).

On the basis of a Raman spectroscopic investigation we have deduced that $Ga_2Br_4.2(dioxane)$ has a structure similar to that of the chloride analogue and the aim of this work is to confirm this deduction.

Using a single crystal sealed in a Lindemann-glass tube, the crystal data were obtained from Weissenberg photographs taken with Cu $K\alpha$ radiation ($\lambda = 1\cdot542$ Å). Intensity measurements were made on a Stoe STADI-2 two-circle automatic diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = $

$0\cdot7107$ Å). On account of the unfavourable orientation of the Lindemann tube relative to the ω axis only layers $l = 0$–4 were measured. The crystals were irregular in shape and the crystal-face development complex so that crystal directions could not be recognized visually and therefore no correction was made for absorption ($\mu = 12\cdot53$ mm⁻¹). The size of the crystal used was $0\cdot21 \times 0\cdot13 \times 0\cdot25$ mm. Scaling of data was carried out with *SHELX* (Sheldrick, 1976); after elimination of those for which $I < 3\sigma(I)$ there remained 1195 unique reflections. An E map obtained with *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1977) revealed the positions of the Ga and Br atoms. These were used to phase $(F_o - F_c)$ maps to give the positions of the remaining atoms (apart from H) using *SHELX*. Full-matrix least-squares refinement with unit weight of all atomic positions, anisotropic U_{ij} values for Ga and Br and isotropic U values for the remaining non-hydrogen atoms was carried out until convergence was reached at $R = 0\cdot0827$. Atomic scattering factors were those of Cromer & Mann (1968) and Cromer & Liberman (1970). Final coordinates and equivalent values (U_{eq}) of the anisotropic temperature coefficients and isotropic (U) values are given in Table 1.*

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters* ($\mathring{A}^2 \times 10^4$)

For Ga and Br atoms $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$.

	x	y	z	U_{eq}/U
Ga(1)	7746 (4)	1009 (2)	4230 (6)	143 (12)
Ga(2)	7766 (3)	2517 (3)	6720 (5)	141 (12)
Br(1)	9929 (3)	3906 (3)	6759 (6)	202 (13)
Br(2)	8473 (4)	−989 (2)	3769 (6)	224 (13)
Br(3)	6881 (4)	1931 (3)	9051 (6)	341 (16)
Br(4)	5718 (4)	952 (4)	3149 (7)	374 (16)
O(1)	9493 (22)	1538 (17)	2511 (34)	194 (50)
O(2)	12016 (25)	2595 (20)	526 (38)	327 (62)
O(3)	6175 (21)	3793 (17)	7133 (33)	155 (46)
O(4)	3870 (26)	5329 (21)	7281 (38)	335 (63)
C(1)	9423 (36)	2744 (26)	2236 (50)	250 (79)
C(2)	10470 (36)	2768 (34)	554 (53)	377 (100)
C(3)	12131 (42)	1419 (30)	798 (54)	368 (98)
C(4)	11125 (33)	1371 (29)	2427 (52)	272 (83)
C(5)	4559 (30)	3352 (25)	7431 (54)	195 (71)
C(6)	3550 (40)	4444 (29)	8263 (54)	352 (94)
C(7)	5480 (36)	5788 (31)	7238 (61)	378 (99)
C(8)	6548 (37)	4737 (27)	6280 (52)	306 (89)
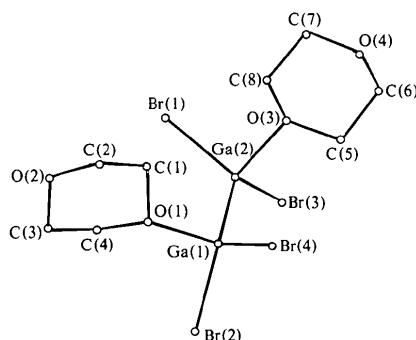
Fig. 1. The structure of $Ga_2Br_4 . 2$(dioxane).

Table 2. *Bond distances* ($\mathring{A}$) *and angles* (°) *around the Ga atoms*

Ga(1)−Ga(2)	2·395 (6)	Ga(1)−Br(2)	2·308 (3)
Ga(1)−Br(4)	2·309 (4)	Ga(1)−O(1)	2·01 (2)
Ga(2)−Br(1)	2·339 (3)	Ga(2)−Br(3)	2·265 (4)
Ga(2)−O(3)	2·04 (2)		

Ga(1)−Ga(2)−Br(1)	118·0 (2)	Ga(1)−Ga(2)−Br(3)	119·1 (2)
Ga(1)−Ga(2)−O(3)	107·5 (8)	Ga(2)−Ga(1)−Br(2)	120·0 (2)
Ga(2)−Ga(1)−Br(4)	118·8 (2)	Ga(2)−Ga(1)−O(1)	106·3 (7)
Br(2)−Ga(1)−Br(4)	109·6 (2)	Br(1)−Ga(2)−Br(3)	110·9 (2)
Br(2)−Ga(1)−O(1)	98·4 (6)	Br(4)−Ga(1)−O(1)	99·1 (7)
Br(1)−Ga(2)−O(3)	97·3 (5)	Br(3)−Ga(2)−O(3)	99·8 (8)

Discussion. The crystal structure determination shows that $Ga_2Br_4 . 2$(dioxane) (Fig. 1) is very similar to the chloride analogue and confirms our previous deductions; bond distances and angles around the Ga atoms are in Table 2. Since we were unable to correct for absorption the e.s.d.'s and R value are higher than expected. The Ga—Ga bond length of 2·395 (6) $\mathring{A}$ compares favourably with other reported values: $Ga_2Cl_6^{2-}$ [2·390 (2) $\mathring{A}$] (Brown & Hall, 1973), $Ga_2Br_6^{2-}$ [2·419 (5) $\mathring{A}$] (Cumming, Hall & Wright, 1974), $Ga_2Cl_4 . 2$(dioxane) [2·406 (1) $\mathring{A}$] (Beamish *et al.*, 1979), $Ga_2Br_4 . 2$(pyridine) [2·421 (3) $\mathring{A}$] (Small & Worrall, 1982). The Ga—Br distances [2·308 (3), 2·309 (4), 2·339 (3) and 2·265 (4) $\mathring{A}$] are shorter than in $Ga_2Br_6^{2-}$ [2·351–2·370 (6) $\mathring{A}$] (Cumming *et al.*, 1974) and $Ga_2Br_4 . 2$(pyridine) [2·350 (2) $\mathring{A}$] (Small & Worrall, 1982) but this is to be expected since in the latter compounds Br atoms on adjacent Ga atoms occupy *trans* positions.

The greater variation in the Ga—Br bond distances compared with the Ga—Cl distances in $Ga_2Cl_4 . 2$(dioxane) is in agreement with Raman studies where more Ga—Br bands are observed in the halogen region of the spectrum.

The torsion angles about Ga(1)—Ga(2) are very similar to those in the chloride complex.*

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* See deposition footnote.

References

BEAMISH, J. C., SMALL, R. W. H. & WORRALL, I. J. (1979). *Inorg. Chem.* **18**, 220–223.

BROWN, K. L. & HALL, D. (1973). *J. Chem. Soc. Dalton Trans.* pp. 1843–1845.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

CUMMING, H. J., HALL, D. & WRIGHT, C. E. (1974). *Cryst. Struct. Commun.* **3**, 107–109.

MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J. P. (1977). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

SHELDRICK, G. M. (1976). *SHELX* 76. Program for crystal structure determination. Univ. of Cambridge, England.

SMALL, R. W. H. & WORRALL, I. J. (1982). *Acta Cryst.* B**38**, 86–87.

TAN, K. H. & TAYLOR, M. J. (1974). *Inorg. Nucl. Chem. Lett.* **10**, 267–270.