The Structure of Bis[dibromo(pyridine)gallium]

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Abstract

$[Ga_2Br_4(C_5H_5N)_2]$, $C_{10}H_{10}Br_4Ga_2N_2$, monoclinic, $C2/m$, $a = 15.79$ (2), $b = 7.772$ (5), $c = 7.586$ (5) Å, $\beta = 113.17$ (3)°, $Z = 2$, $D_x = 2.394$, $D_m = 2.38$ Mg m^{-3}. The structure has been solved from 622 diffractometer-measured intensities with Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å) and refined by full-matrix least squares to $R = 0.0496$. The complex is a discrete molecule containing a Ga–Ga bond of length 2.421 (3) Å and it adopts the *trans* configuration.

Introduction

We have recently reinvestigated a number of complexes formed between the mixed-oxidation-state gallium halides Ga_2X_4 and a variety of ligands. Previous work has shown that there are two main classes of compound formed with N, O, S and Se donors (Ali, Brewer, Chadwick & Garton, 1959; Brewer, Chadwick & Garton, 1961): (1) $Ga_2X_4.4L$ (L a monodentate ligand), formulated $GaL_4^+.GaX_4^-$; (2) $Ga_2X_4.2L$ (L a bidentate ligand), formulated $GaL_2^+.GaX_4^-$.

The ionic nature of class (2) is in doubt since we have shown that the 1,4-dioxane complex $Ga_2Cl_4.$-2(dioxane) is a discrete molecule and contains a Ga–Ga bond (Beamish, Small & Worrall, 1979). We are presently looking at other members of the class to see if this result is general. The $Ga_2Cl_4.$2(dioxane) complex is interesting since dioxane behaves as a monodentate ligand and this suggests that there should exist a series of similar metal–metal-bonded complexes of the same stoichiometry with genuine monodentate ligands. We have now prepared several complexes of this type and below describe the preparation and crystal structure of $Ga_2Br_4.$2(pyridine).

Experimental

Previous work has shown that pyridine complexes may not be prepared by direct reaction between the halides and ligand, possibly because of the reduction of pyridine by Ga$^+$ (Ali *et al.*, 1959). We have found that they may be readily prepared from dioxane complexes by ligand-replacement reactions. An excess of dry pyridine was condensed on to $Ga_2Br_4.$2(dioxane) which was prepared by the method previously described (Beamish *et al.*, 1979). On removal of the liquid a white powder remained which analysed as $Ga_2Br_4.$-2(pyridine). Analysis: found Ga 22.8, Br 51.5%; calculated Ga 22.6, Br 51.8%. The preparation was carried out in an all-glass apparatus *in vacuo* and subsequent manipulations were carried out in a nitrogen-filled dry box because of the susceptibility of the complex to moisture. Crystals were obtained from pyridine solutions and the density was determined by flotation in a 1,2-dibromoethane/benzene mixture.

Crystallographic measurements

Using a single crystal 0.19 × 0.16 × 0.42 mm, sealed in a Lindemann-glass tube, the crystal data were obtained from Weissenberg photographs taken with Cu $K\alpha$ radiation ($\lambda = 1.542$ Å). Intensity measurements were made on the Stoe STADI-2 two-circle automatic diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Layers $l = 0$–8 with the crystal set about **c** were measured. Absorption corrections ($\mu = 12.2$ mm^{-1}) and scaling of data were carried out with *SHELX* (Sheldrick, 1976); after elimination of those for which $I < 3\sigma(I)$ there remained 622 unique reflections. An E map obtained by the *MULTAN* 78 program (Main, 1978) revealed the positions of the Ga

Table 1. *Fractional atomic coordinates* (×10⁴) *and equivalent isotropic thermal parameters* (×10⁴)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U_{eq} (Å²)
N	1832 (8)	5000†	873 (18)	402 (60)
C(1)	2675 (11)	5000†	2387 (27)	623 (102)
C(2)	3481 (11)	5000†	2003 (28)	660 (106)
C(3)	3432 (12)	5000†	117 (28)	627 (106)
C(4)	2552 (14)	5000†	−1421 (35)	857 (137)
C(5)	1756 (12)	5000†	−935 (29)	681 (111)
Ga	688 (1)	5000†	1464 (2)	398 (10)
Br	907 (1)	2588 (2)	3463 (2)	672 (9)

† Constrained.

and Br atoms; $(F_o - F_c)$ maps then gave the positions of the remaining atoms (apart from H) using *SHELX*. Using unit weights, full-matrix least-squares refinement of all atomic positions and anisotropic U_{ij} values was carried out until convergence was reached at $R = 0.0496$. Atomic scattering factors were those of Cromer & Mann (1968) and Cromer & Liberman (1970). Final coordinates and equivalent values (U_{eq}) of the anisotropic temperature factors are given in Table 1.*

Discussion

$Ga_2Br_4.2(C_5H_5N)$ exists as a single discrete molecule with a Ga—Ga bond and a *trans* configuration (Fig. 1); bond distances and angles are listed in Table 2. The Ga—Ga bond length is 2·421 (3) Å and is longer than that found in the only other comparable neutral complex reported, $Ga_2Cl_4.2$(dioxane) [2·406 (1) Å] (Beamish *et al.*, 1979). It compares favourably with the Ga—Ga distance observed in the anion $Ga_2Br_6^{2-}$ [2·419 (5) Å] (Cumming, Hall & Wright, 1974). Comparison of other bond parameters with this ionic

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36236 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
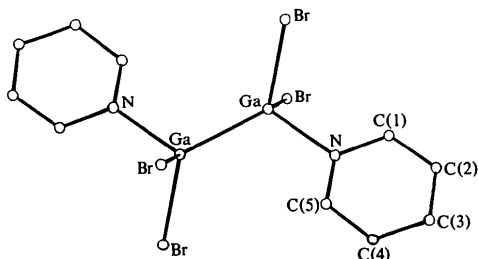

Fig. 1. The molecular structure of $Ga_2Br_4.2(C_5H_5N)$.
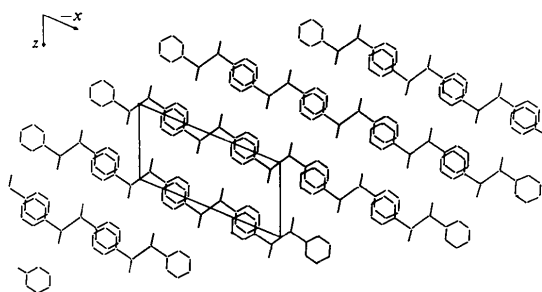
Fig. 2. Arrangement of $Ga_2Br_4.2(C_5H_5N)$ molecules in the crystal.

Table 2. *Bond distances* (Å) *and angles* (°)

Ga—Br	2·350 (2)	Ga—Ga	2·421 (3)
Ga—N	2·024 (11)	N—C(1)	1·37 (2)
C(1)—C(2)	1·41 (2)	C(2)—C(3)	1·40 (2)
C(3)—C(4)	1·42 (3)	C(4)—C(5)	1·44 (2)
C(5)—N	1·33 (2)		

Br—Ga—Br	105·8 (1)	Br—Ga—N	103·0 (2)
Ga—Ga—Br	116·3 (1)	Ga—Ga—N	110·8 (2)
N—C(1)—C(2)	119 (2)	C(1)—C(2)—C(3)	121 (2)
C(3)—C(4)—C(5)	117 (2)	C(4)—C(5)—N	122 (2)
C(5)—N—C(1)	122 (1)	C(2)—C(3)—C(4)	118 (2)

species shows close agreement for Ga—Br distances and Br—Ga—Br bond angles: 2·350 (2) Å [2·351–2·370 (6) Å]; 105·8 (1)° [104·0–105·3 (2)°]. The neutral complex may be regarded as a derivative of the anion, which has a staggered structure, by replacement of two *trans* Br atoms by pyridine. This results in an increase in the Ga—Ga—Br angle [113·7–114·1 (2)°] to 116·3 (1)°.

All atoms in the asymmetric unit apart from Br lie on a mirror plane and the molecule has $2/m$ (C_{2h}) symmetry (by space-group requirement). The observed *trans* configuration is different from that adopted by $Ga_2Cl_4.2$(dioxane) and this may be ascribed to the ease of stacking of planar pyridine rings compared to the dioxane chairs. A chain-like structure (Fig. 2) is formed by the overlap of pyridines on adjacent molecules, the rings being separated by ~3·89 Å $(b/2)$.

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