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Cogent Chemistry (2016), 2: 1273065



Received: 22 November 2016  
Accepted: 13 December 2016  
First Published: 22 December 2016

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Reviewing editor:  
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# Crystal structure of bis(triphenylphosphonium) hexabromodigallate(II) in the correct space group: Conformational complexity in a heteroethane

Olivia N.J.M. Marasco<sup>1</sup>, Sydney K. Wolny<sup>1</sup>, Jackson P. Knott<sup>1,2</sup>, Daniel Stuart<sup>1,2</sup>, Tracey L. Roemmele<sup>1,2</sup> and René T. Boéré<sup>1,2\*</sup>

**Abstract:** The crystal structure of  $[\text{Ph}_3\text{PH}]_2[\text{Ga}_2\text{Br}_6]$ , previously described as having a disordered anion in the space group  $R\bar{3}$ , has been re-determined in the correct space group  $P\bar{3}$ , where it is fully ordered. Interestingly, two-thirds of the  $[\text{Ga}_2\text{Br}_6]^{2-}$  dianions have an intermediate conformation with a Br–Ga–Ga–Br torsion angle of  $36.91(1)^\circ$ , while the remaining is staggered as required from adopting a site with inversion symmetry. In the lattice,  $[\text{Ph}_3\text{PH}]^+$  ions lie along the same threefold axes as the dianions and are oriented such that the P–H bond is directed towards a gallium atom. The phosphonium ions lie back-to-back and interact with relatively strong T-interactions between phenyl rings on adjacent cations. DFT calculations at the B3LYP/6–311+G(fd,) level have been used to determine the barriers to rotation in  $[\text{Ga}_2\text{X}_6]^{2-}$  ions. For  $\text{X} = \text{Cl}$  and  $\text{X} = \text{Br}$ , the barriers are found to be very small, with values of 4.3 and 5.1  $\text{kJ mol}^{-1}$  for the two halogens.

**Subjects:** Computational and Theoretical Chemistry; Inorganic Chemistry; Crystallography

**Keywords:** hexahalodigallate; sextuple phenyl embrace; single bond rotation; conformation; X-ray crystal structure; density functional theory calculations

### 1. Introduction

Gallium is most stable in the Ga(III) oxidation state while Ga(I) is also accessible (Lichtenthaler et al., 2015). By contrast, Ga(II) is rare except in dimers or oligomers (Evans & Taylor, 1969; Kloo, Rosdahl, & Taylor, 2002). The hexahalodigallates,  $[\text{Ga}_2\text{X}_6]^{2-}$ , have long been known as heavy analogues to substituted ethanes. Tuck (Windsor, Canada) and Taylor (Auckland, NZ) pioneered an elegant

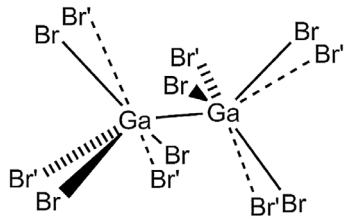
### ABOUT THE AUTHOR

René T. Boéré has taught in all areas of main group element chemistry and employs a research strategy of chemical synthesis underpinned by detailed spectroscopic and structural investigation. Solid-state structures determined by single-crystal X-ray diffraction methods are central to most of his research. He has a special interest in main-group element free radicals and hence in unusual oxidation states where radical species can be expected, such as gallium(II). He also seeks to place all his results into a broad theoretical framework for which he makes extensive use of computational methods—most often hybrid density-functional theory.

### PUBLIC INTEREST STATEMENT

Data repositories have become of great significance in scientific research with the advent of affordable storage and the WWW for accessing information remotely. Of key importance in structural chemistry is the Cambridge Structure Database, which comprises over 850,000 entries from X-ray and neutron diffraction analyses and provides 3D geometrical parameters. Analyses of this data are only as good as the quality of the underlying information, and erroneous entries can impact the validity of conclusions based thereon. This article provides a corrective to an earlier result contained in the CSD that overemphasizes the prevalence of one particular form of hexahalodigallate anions.

**Figure 1. Disordered  $[\text{Ga}_2\text{Br}_6]^{2-}$  anion in the refinement model for FUPSIS.**



electrochemical preparative method for several salts thereof (Khan, Oldham, Taylor, & Tuck, 1980; Khan, Tuck, Taylor, & Rogers, 1986; Taylor & Tuck, 1983). The earliest crystal structure of a hexabromodigallate(II) to have entered the literature is the tetra-*n*-propylammonium salt (Cambridge Structure Database, CSD, refcode: PRAMBG; Cumming, Hall, & Wright, 1974; Groom & Allen, 2011). The ion has also been identified in a binary phase,  $\text{Ga}_2\text{Br}_3$  (Hönle, Gerlach, Weppner, & Simon, 1986) and a closely-related ternary phase,  $\text{LiGaBr}_3$  (Hönle & Simon, 1986). An unusual salt with *hexakis*-(*N,N*-dimethylformamide-*O*)-gallium(III) counter ions was isolated from a DMF extraction of a product obtained from oxidation of  $\text{GaBr}$  (refcode: FECSUG) (Duan & Schnöckel, 2004). The crystal structure of the title compound was first reported in 1986 along with its chloride and iodide analogues (Khan et al., 1986). In this original report, the authors stated “beyond doubt ... a slight imperfection in the halogen atom positions caused a lowering of the symmetry to the space group  $P\bar{3}$ ”. However, the structure was unable to be solved in this lower symmetry space group due to insufficient measured reflections, and therefore the models were refined in the higher symmetry space group  $R\bar{3}$ . This structure (refcode: FUPSIS) is compiled in the CSD but the *apparent* 33% disorder in the bromine atom positions (Figure 1) has been suppressed. The Br–Ga–Ga–Br’ torsion angle between the ordered and disordered halogens is about  $44.2^\circ$  whereas Br–Ga–Ga–Br is  $60^\circ$  (exact by symmetry).

Interest remains strong in the chemistry of various  $[\text{Ga}_2\text{X}_6]^{2-}$  salts.  $[\text{N}^n\text{Pr}_4]_2[\text{Ga}_2\text{Cl}_6]$ , refcode: TMAGAC (Brown & Hall, 1973) and  $[\text{Ph}_3\text{PH}]_2[\text{Ga}_2\text{Cl}_6]$ , refcode: FUPSIS (Khan et al., 1986) have been joined more recently by a salt of the mixed-halogen species  $[\text{Ga}_2\text{I}_5\text{Cl}]^{2-}$ , refcode: BAZTIH (Yurkerwich, Yurkerwich, & Parkin, 2011). Structures of various  $[\text{Ga}_2\text{I}_6]^{2-}$  salts include FUPSEO (Khan et al., 1986), FASSOI (Tian, Pape, & Mitzel, 2004) and ISILEB (Baker, Jones, Kloth, & Mills, 2004). In the mixed-substituent anion  $[\text{Ga}_2\text{I}_5(\text{nhc})]^-$ , refcode OJAWEB, one iodide is replaced by a neutral *N*-heterocyclic carbene (Baker, Bettentrup, & Jones, 2003). There is also an extensive chemistry of  $\text{LX}_2\text{Ga}-\text{GaX}_2\text{L}$  species with a wide range of neutral ligands L, all of which have Ga–Ga single bonds (selected references include: Baker, Bettentrup, & Jones, 2004; Ball, Cole, & McKay, 2012; Beagley et al., 1996; Duan & Schnöckel, 2004; Gordon et al., 1997; Nogai & Schmidbaur, 2002, 2004; Rickard, Taylor, & Kilner, 1999; Small & Worrall, 1982; Worrall & Small, 1982).

In the course of preparing the title compound,  $[\text{Ph}_3\text{PH}]_2[\text{Ga}_2\text{Br}_6]$ , we elected to obtain a low temperature crystal structure using a modern area-detector diffractometer to address the reported structural anomaly. We are now able to confirm the hypothesis of Khan et al. that the trigonal space group  $P\bar{3}$  is correct. Furthermore, in this structural model, the bromine atom positions are fully ordered in two *independent*  $[\text{Ga}_2\text{Br}_6]^{2-}$  ions which differ significantly in conformation about the Ga–Ga bond. One such molecule is perfectly staggered as required from its location at a site with crystallographic inversion symmetry, whereas a second molecule is in an intermediate conformation with a Br–Ga–Ga–Br torsion angle of  $36.91(1)^\circ$ . This observation raises questions about the nature of conformational isomerism in hexahalodigallates(II), which is the subject of this report.

## 2. Results and discussion

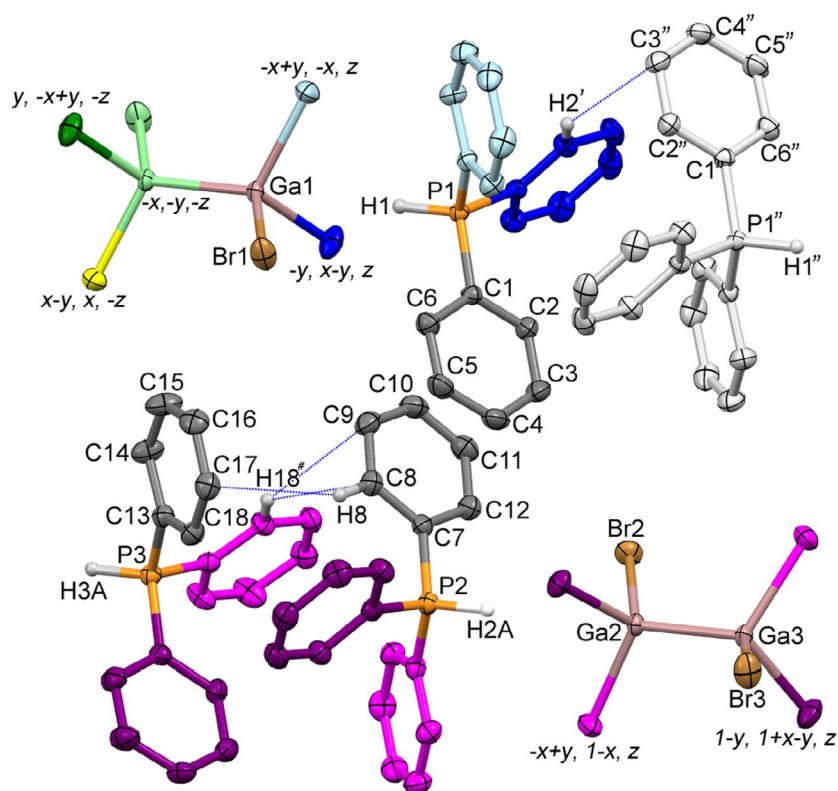
The title complex,  $[\text{Ph}_3\text{PH}]_2[\text{Ga}_2\text{Br}_6]$ , was synthesized through direct electrochemical synthesis from elemental gallium by a variation on an optimized method (Taylor & Tuck, 1983). Under the acidic conditions, the added  $\text{Ph}_3\text{P}$  is protonated to provide an exceptional counterion for the trigonally symmetric anion and consequently crystals of  $[\text{Ph}_3\text{PH}]_2[\text{Ga}_2\text{Br}_6]$  form during constant-current

electrolysis. Crystals filtered from the solution were found to include exemplars suitable for an X-ray diffraction analysis. Characterization was achieved by melting point and vibrational spectroscopy. Fourier transform infra-red (FTIR) and Raman vibrational spectra are in excellent agreement with the literature (Khan et al., 1986). In the Raman spectrum, the  $\nu(\text{P-H})$  band is found to be split into a doublet of 2,374 and 2,387  $\text{cm}^{-1}$  (lit. 2,374 and 2,384  $\text{cm}^{-1}$ ). The deformation band is found at 869  $\text{cm}^{-1}$  (lit. 870  $\text{cm}^{-1}$ ). The crucial, very intense  $A_{1g}$  combination  $\nu(\text{Ga-Br})/\nu(\text{Ga-Ga})$  band that is characteristic for a Ga-Ga single bond in all  $\text{LX}_2\text{Ga-GaX}_2\text{L}$  and  $[\text{X}_3\text{Ga-GaX}_3]^{2-}$  species (Beamish, Boardman, Small, & Worrall, 1985) is found at 165.7  $\text{cm}^{-1}$  (lit. 164  $\text{cm}^{-1}$ ).

### 2.1. Crystal structure determination

The crystal structure was successfully refined in the centrosymmetric trigonal space group  $P\bar{3}$  (Figure 2 and Table 1). One  $[\text{Ga}_2\text{Br}_2]^{2-}$  anion (Ga1;Br1) and one  $[\text{Ph}_3\text{PH}]^+$  cation (P1) lie along the unique  $\bar{3}$  axis; this anion is centred on Wyckoff position 1a with  $\bar{3}$  site symmetry (so that the geometry is perfectly staggered), whereas the cation occupies Wyckoff position 2c with threefold rotational symmetry. The second  $[\text{Ga}_2\text{Br}_2]^{2-}$  anion (Ga2,3;Br2,3) and two  $[\text{Ph}_3\text{PH}]^+$  cations (P2,3) lie along the two threefold axes in the unit cell and all occupy Wyckoff positions 2d with site symmetries of 3. This anion has a smallest Br-Ga-Ga-Br torsion angle of 36.91 (1)°, so that it is almost half way between staggered and eclipsed. Symmetry related atoms with the same label are distinguished by colour coding in Figure 2. The P-H bonds of all the cations are directed towards Ga centres, whilst two  $\text{Ph}_3\text{PH}^+$  moieties associate back-to-back, allowing their three phenyl rings to associate through phenyl carbon/phenyl hydrogen T-interactions. This association is reminiscent of the supramolecular organization of  $\text{Ph}_4\text{P}^+$  cations which has been dubbed the “sextuple phenyl embrace” with estimated attraction energy of 60–85  $\text{kJ mol}^{-1}$  (Dance & Scudder, 1996). Similar contacts have been noted in dimers of  $\text{SbPh}_3$  in a recent aromatic adduct structure, with  $\text{CH}\cdots\text{C}_{\text{aromatic}}$  short contacts of 2.915–2.995 Å (Boeré, 2016). In the title structure, the T-interactions have lengths of 2.936 Å [ $\text{C3}\cdots\text{H2}' (-y, x-y, z)$ ] on the  $\bar{3}$  axis and on the 3 axis of 2.885 [ $\text{C17}\cdots\text{H8}$ ], 2.995 [ $\text{C8}\cdots\text{H18}'' (-x+y, 1-x, z)$ ] and 2.961 [ $\text{C9}\cdots\text{H18}^{\#} (-x+y, 1-x, z)$ ] Å. The T-interactions in the P1 cations and the two T-interactions in the P2,3 cations are replicated by the 3-fold rotational symmetry; these are not shown in Figure 2 to avoid additional

**Figure 2.** Displacement ellipsoids (50% probability) plot of the asymmetric unit depicting the molecular structures of the two independent  $[\text{Ga}_2\text{Br}_2]^{2-}$  anions and the three independent  $[\text{Ph}_3\text{PH}]^+$  cations (Ga1 with site symmetry  $\bar{3}$ ; Ga2,3 with site symmetry 3). False colours indicate symmetry-related atoms (sym codes on diagram). A symmetry-equivalent P1 cation additional to the asymmetric unit is shown in light grey (“). Phenyl ring T-interactions from C-H to C are shown with dashed blue lines *once* for each symmetry-replicated interaction. H atoms on carbon are omitted, as are atom labels for symmetry related atoms.





**Table 1. Selected interatomic distances, angles and torsions in the crystal structure of the title compound**

Atoms	Distance (Å)	Atoms	Angle (°)	Atoms	Dihedral (°)
Ga1–Ga1 <sup>i</sup>	2.4124 (7)	Br1–Ga1–Ga1 <sup>i</sup>	115.115 (9)	Br1–Ga1–Ga1 <sup>i</sup> –Br1 <sup>vii</sup>	60 (exact)
Br1–Ga1	2.3732 (3)	Br1–Ga1–Br1 <sup>iv</sup>	103.284 (11)	Br2–Ga2–Ga3–Br3 <sup>viii</sup>	36.91 (1)
Ga2–Ga3	2.3978 (5)	Br2–Ga2–Ga3	113.700 (9)	C1–P1...P <sup>ix</sup> –C1 <sup>ix</sup>	60 (exact)
Br2–Ga2	2.3731 (3)	Br3–Ga3–Ga2	114.136 (9)	C7–P2...P3–C13 <sup>x</sup>	55.60 (1)
Br3–Ga3	2.3770 (3)	Br2–Ga2–Br2 <sup>v</sup>	104.931 (11)		
P1–C1	1.7794 (19)	Br3 <sup>vi</sup> –Ga3–Br3	104.431 (11)		
P1–H1	1.321 (18)	C1–P1–C1 <sup>vii</sup>	110.04 (6)		
P2–C7	1.785 (2)	C1–P1–H1	108.90 (7)		
P2–H2A	1.314 (18)	C7–P2–C7 <sup>v</sup>	111.09 (6)		
P3–C13	1.780 (2)	C7–P2–H2A	107.80 (7)		
P3–H3A	1.304 (18)	C13 <sup>vi</sup> –P3–C13	109.57 (7)		
Ga1...P1	4.518 (1)	C13–P3–H3A	109.37 (7)		
P1...P1 <sup>ii</sup>	6.156 (1)				
Ga2...P2	4.604 (1)				
Ga3...P3 <sup>iii</sup>	4.460 (2)				
P2...P3	6.145 (1)				

<sup>i</sup>–x, –y, –z.

<sup>ii</sup>–x, –y, 1 – z.

<sup>iii</sup>x, y, 1 + z.

<sup>iv</sup>–y, x – y, z.

<sup>v</sup>–y + 1, x – y + 1, z.

<sup>vi</sup>–x + y, 1 – x, z.

<sup>vii</sup>y, –x + y, z. –x.

<sup>viii</sup>–x + y, 1 – x, z.

<sup>ix</sup>–x, –y, 1 – z.

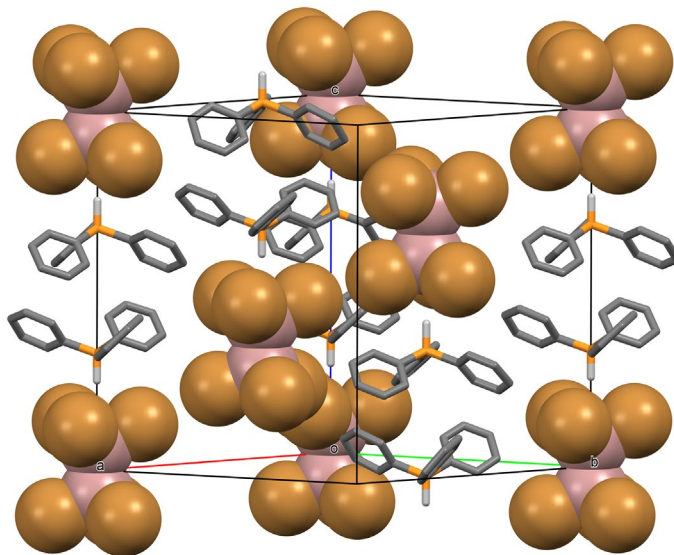
<sup>x</sup>–x + y, 1 – x, z.

clutter. The C1–P1...P1'–C1' torsion angle between two such interlocked phosphonium ions is 60° (exact by lattice symmetry) for the P1 ions at Wyckoff position 2c, while the C7–P2...P3–C13 torsion is 55.60 (1)° for the pair of phosphonium ions occupying Wyckoff position 2d.

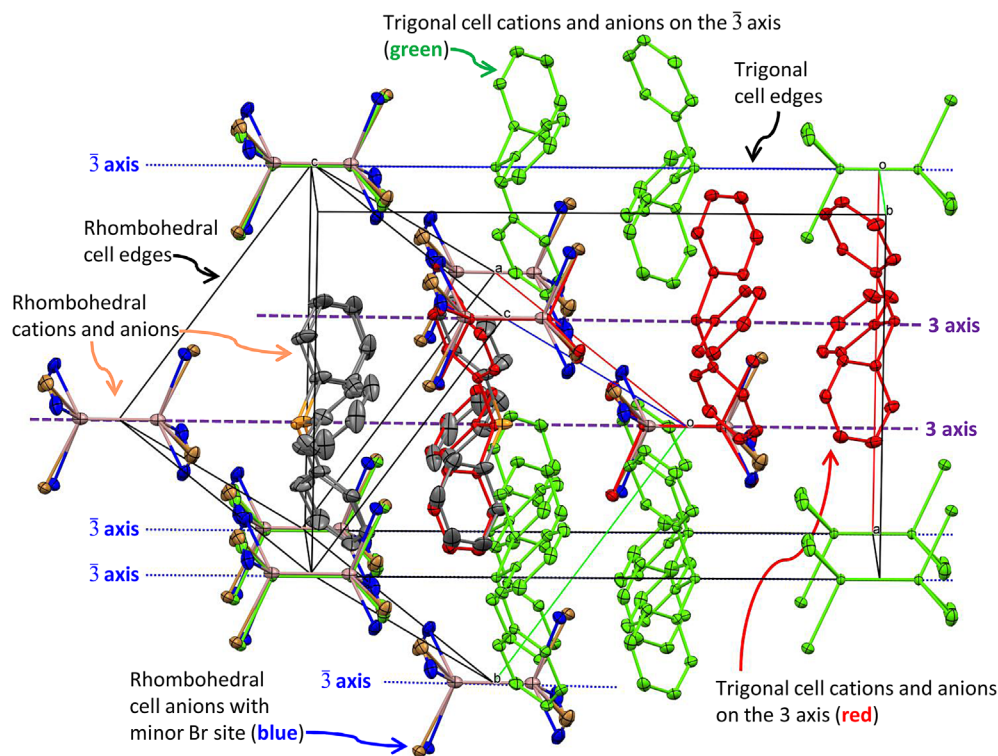
The intriguing packing arrangement is well-suited to the cylindrical “dumbbell”-shaped [Ga<sub>2</sub>Br<sub>6</sub>]<sup>2-</sup> anions and the propeller-shaped phosphonium cations as depicted in a space filling diagram in Figure 3. The “vertical” columns of Ph<sub>3</sub>PH<sup>+</sup>—[Ga<sub>2</sub>Br<sub>6</sub>]<sup>2-</sup>—HPPH<sub>3</sub> ions along the 3 and  $\bar{3}$  axes are close-packed but alternate out of register by approximately half the unit cell c distances. Consequently, each [Ga<sub>2</sub>Br<sub>6</sub>]<sup>2-</sup> dimer is surrounded on six sides by phenyl ring C–H atoms of the two phosphonium ions.

In order to compare to the previously reported structure model (refcode: FUPSIS), especially to check whether the difference in refined models might have been caused by the change in temperature from ambient to 100 K in our data-set, we also refined our structure in space group  $R\bar{3}$ . Very close agreement is found for the anion to that in FUPSIS, and specifically the Br–Ga–Ga–Br' torsion angle to the disordered site is about 40.0°. Thus, there is no evidence for a phase change having occurred over the temperature interval between the earlier structure and this determination. In Figure 4, our disordered model is superimposed on the true structure with the rhombohedral body diagonal oriented along the ( $\frac{2}{3}$   $\frac{1}{3}$  0) 3 axis in the  $P\bar{3}$  unit cell. Although the ratio of staggered GaBr<sub>3</sub> entities on the  $\bar{3}$  axis and intermediate conformation entities on the 3 axis of the true structure is actually 1:2, there is a virtual coincidence of Br atom positions of the  $R\bar{3}$  model with the Br2 atom in the  $P\bar{3}$  unit cell, so that the apparent disorder population observable in the  $R\bar{3}$  refinement is expected to be

**Figure 3. Packing diagram of the structure of the title compound in  $P\bar{3}$ . H atoms on the phenyl rings are omitted for clarity, as are all atoms along the front (1 1 0) unit cell edge. The phosphonium ions are rendered as rods, whereas the hexabromodigallate ions are rendered as “space filling” spheres.**



**Figure 4. Overlaid unit cells of the title structure in  $P\bar{3}$  with the alternate refinement in  $R\bar{3}$  with apparent disorder as in (Khan et al., 1986), drawn as 30% displacement ellipsoids. The  $\bar{3}$  body diagonal of the rhombohedral cell is aligned with the 3 axis of the trigonal cell along  $(\frac{2}{3} \frac{1}{3} 0)$ .**



0.333. Freely refining the occupancies resulted in 0.375, in excellent agreement with this prediction (Khan et al., 1986). The disorder model they reported ignored the fates of the  $\text{Ph}_3\text{PH}^+$  ions, implying that these ions are ordered. However, as can be seen in Figure 4, the displacement ellipsoids of the P and C atoms of this ion in the  $R\bar{3}$  refinement are all severely distorted. In fact, both the positions of the atoms along the c axis and the rotational displacements around the 3 and  $\bar{3}$  axes in the true structure are different for the independent phosphonium ions.

The small C7–P2...P3–C13 torsion angle of 55.60 (1)° seems to be associated with a shorter T-interaction in this pair than is observed for the ions on the  $\bar{3}$  axis (Figure 4). This raises the distinct possibility that it is the stronger phosphonium ion intermolecular interactions that provide a driving force for adoption of the lower symmetry space group, thereby possibly inducing the intermediate conformation in the hexabromodigallate on the  $\bar{3}$  axis through interactions between the phenyl rings and the digallate bromine atoms. Importantly, the *spacing* of the  $\text{Ph}_3\text{PH}^+[\text{Ga}_2\text{Br}_6]^{2-} \text{HPPH}_3$  ions along the  $\bar{3}$  axes are symmetrical as required by lattice symmetry, with  $\text{Ga1}\cdots\text{P1} = 4.518$  (1) Å. However, along the  $\bar{3}$  axis the spacing is long-short-long, with  $\text{Ga2}\cdots\text{P2} = 4.604$  (1) and  $\text{Ga3}\cdots\text{P3}' = 4.460$  (2) Å. It is this asymmetry that allows the P2...P3 distance to be 0.011 (1) Å shorter than P1...P1', with the aforementioned lower C–P...P–C' torsion angle and stronger T-interactions.

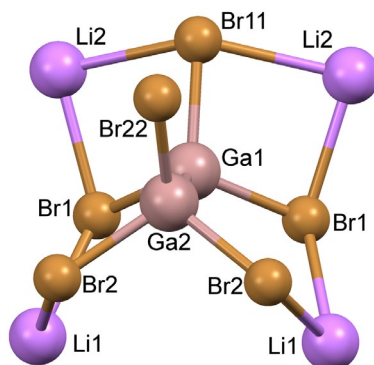
In summary, the crystal structure in the correct space group of the title compound holds several surprises. First, only one-third of the lattice occupancy of  $[\text{Ga}_2\text{Br}_6]^{2-}$  ions is in the “expected” staggered geometry, whilst the remaining two-thirds are in an intermediate conformation. Secondly, the phosphonium ions on the  $\bar{3}$  axis, also two-thirds of the total occupancy, relax by twisting so as to maximize the “sextuple phenyl embrace”, providing a possible driving force for adoption of the lower symmetry crystal lattice.

In the crystal structure of  $[\text{N}^n\text{Pr}_4]_2[\text{Ga}_2\text{Br}_6]$ , refcode: PRAMBG, the dianion has crystallographically required  $\bar{1}$  site symmetry, rendering it staggered (Cumming et al., 1974). However, the  $[\text{Ga}_2\text{Br}_6]^{2-}$  ions in binary and ternary solid phases, best formulated as  $\text{Ga}_2[\text{Ga}_2\text{Br}_6]$  (Hönle et al., 1986) and  $\text{Li}_2[\text{Ga}_2\text{Br}_6]$  (Hönle & Simon, 1986), surprisingly crystallize in eclipsed conformations. The structures of the two phases are different, but in both the  $\text{M}^+$  counter ions are also strongly coordinated with the bromide ions, including bridges across the two Ga(II) atoms of the *same* ion. The point can be illustrated by considering the structure of  $\text{Li}_2[\text{Ga}_2\text{Br}_6]$  (Figure 5). This shows that Li1 doubly bridges the eclipsed  $[\text{Ga}_2\text{Br}_6]^{2-}$  anion, whereas Li2 is chelated by the  $\text{GaBr}_3$  triad. These interactions could be the driving force for a potentially higher energy conformation of the anions. These authors commented that conformational changes in  $[\text{Ga}_2\text{Br}_6]^{2-}$  are apparently quite small. In the more recently reported salt  $[\text{Ga}(\text{O}-\text{DMF})_6]_2[\text{Ga}_2\text{Br}_6]$  (refcode: FECSUG) the cations are unable to interact strongly with the anion bromine atoms (Duan & Schnöckel, 2004). In this structure, one half of the  $[\text{Ga}_2\text{Br}_6]^{2-}$  ions are staggered by imposed  $\bar{1}$  site symmetry whilst the remainder have intermediate conformations, with a smallest torsion angle of 47.1°, so quite similar to what occurs in the structure of  $[\text{Ph}_3\text{PH}]_2[\text{Ga}_2\text{Br}_6]$  in the correct space group.

## 2.2. Computed conformational energy profile

In order to address this structural diversity, we have undertaken DFT calculations at the B3LYP/6-311+G(fd,) level of theory. If the intermediate geometry from the title structure is geometry-optimized, it is found to reorganize during the calculations to a perfectly staggered conformation. This is, as expected for an ethane-like molecule, the most stable conformation. In order to ascertain approximate energies for such a transformation, a series of calculations were undertaken that scan the conformational coordinate from 63.3° to 183.3° in  $[\text{Ga}_2\text{X}_6]^{2-}$  (X = Cl, Br). The results, shown in

**Figure 5.** Representation of part of the crystal structure of  $\text{Li}_2[\text{Ga}_2\text{Br}_6]$ ; there is a mirror plane through Br11, Ga1, Ga2, Br22.  $\text{Li}^+$  ions coordinated to Br22 and all remaining bromine atoms completing the coordination spheres of Li1,2 have been omitted for clarity. The data is taken from Hönle and Simon (1986).



**Figure 6. Conformational energy profile for the title anion computed at the B3LYP/6-311+G(fd,) level of theory for gas-phase  $[\text{Ga}_2\text{Cl}_6]^{2-}$  and  $[\text{Ga}_2\text{Br}_6]^{2-}$  ions. The calculations were undertaken in  $10^\circ$  steps in the X-Ga-Ga-X torsion angle starting from  $63.3^\circ$ .**

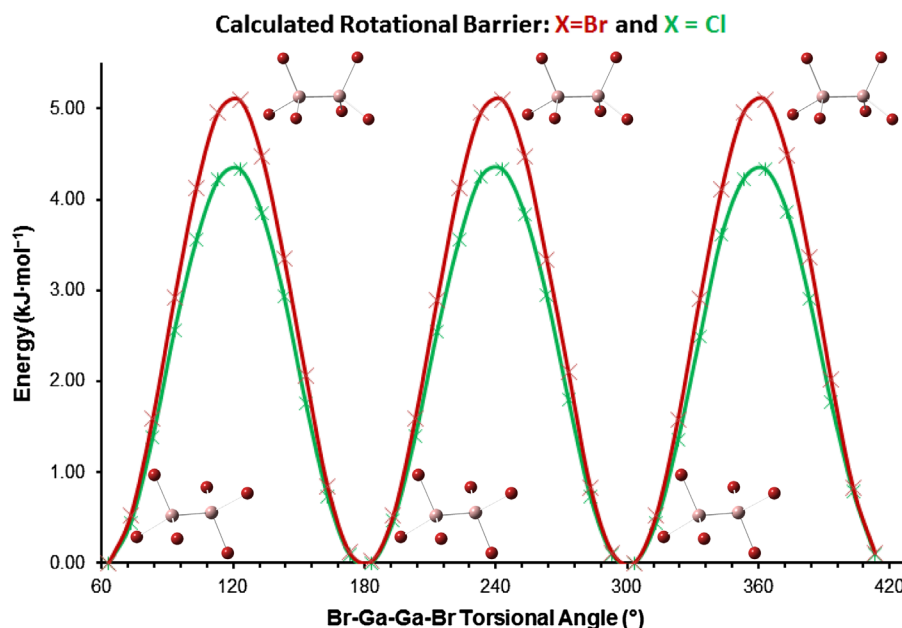


Figure 6, indicate (1) that the staggered conformation is indeed the lower energy preferred geometry and (2) that the energetic cost of adopting the most hindered eclipsed conformation is very small, on the order of just  $5 \text{ kJ mol}^{-1}$ . The intermediate conformation encountered for two-thirds of the anions in the title crystal structure has no significance in the calculated profiles.

The rotational barrier in the title anion is surprisingly small, which is consistent with crystallographic characterization of eclipsed and intermediate forms in addition to the preferred staggered conformation amongst the small series of extant structurally characterized salts. To our knowledge, no experimental or calculated barriers to rotation have been reported for hexahalodigallate dianions. However, there is an intense interest in the barrier to rotation for the neutral Group 14 element ethane-like species (Cortés-Guzmán, Cuevas, Pendás, & Hernández-Trujillo, 2015; Johansson & Swart, 2013; Mo & Gao, 2007; Morino & Hirota, 1958; Quijano-Quiñones, Quesadas-Rojas, Cuevas, & Mena-Rejón, 2012). Table 2 contains data on some of these species. First of all, the barrier in ethane itself is known to be  $12.8 \text{ kJ mol}^{-1}$ , three times as high as in the title anion. However, upon progressing to the hydrides of the third and fourth period analogues, this value drops dramatically to only  $3.1 \text{ kJ mol}^{-1}$  for  $\text{H}_3\text{GeGeH}_3$ . Similarly, whilst the measured barrier heights in hexachloro- and hexabromoethanes rise dramatically to  $>73$  and  $>83 \text{ kJ mol}^{-1}$ , the barrier in  $\text{Cl}_3\text{SiSiCl}_3$  is measured to be only  $4.2 \text{ kJ mol}^{-1}$ . Evidently, the much larger radius of Ga is more than enough to offset the large size of the six bromide substituents, so that the barrier height in  $[\text{Ga}_2\text{Br}_6]^{2-}$  is quite similar to that in  $\text{Cl}_3\text{SiSiCl}_3$ .

**Table 2. Experimental or calculated barriers to rotation in  $[\text{X}_3\text{EEX}_3]$  species**

Molecule	Exp/calc	kJ/mol	References
$\text{H}_3\text{CCH}_3$	c	12.8	Mo and Gao (2007)
$\text{H}_3\text{SiSiH}_3$	c	4.1	Mo and Gao (2007)
$\text{H}_3\text{GeGeH}_3$	c	3.1	Mo and Gao (2007)
$\text{H}_3\text{CSiH}_3$	c	6.1	Mo and Gao (2007)
$\text{Cl}_3\text{CCCl}_3$	e	73.2	Morino and Hirota (1958)
$\text{Br}_3\text{CCBr}_3$	e	83.7	Morino and Hirota (1958)
$\text{Cl}_3\text{SiSiCl}_3$	e	4.2	Morino and Hirota (1958)
$[\text{Ga}_2\text{Cl}_6]^{2-}$	c	4.34	This work
$[\text{Ga}_2\text{Br}_6]^{2-}$	c	5.09	This work



$\text{Ge}_2\text{Br}_6$  remains an under-investigated compound (Curtis & Wolber, 1972; Höfler & Brandstätter, 1975). Although it can be made as an air-sensitive colourless compound, it is unstable towards decomposition to  $\text{GeBr}_2$  and  $\text{GeBr}_4$  above  $85^\circ\text{C}$  (Curtis & Wolber, 1972). In the solid state, it may crystallize centrosymmetrically based on the non-coincidence of IR and Raman bands in its vibrational spectrum (Curtis & Wolber, 1972) but no crystal structure has been reported for this species. The  $\nu(\text{Ge}-\text{Ge})$  band was measured to be  $196\text{ cm}^{-1}$  (Höfler & Brandstätter, 1975), implying a Ge-Ge bond that is somewhat stronger than the Ga-Ga bonds in digallates ( $\nu(\text{Ga}-\text{Ga}) = 165.7\text{ cm}^{-1}$ ). Both  $\text{Br}_3\text{SiSiBr}_3$  ( $2/m$  site symmetry) and  $\text{I}_3\text{SiSiI}_3$  ( $\bar{3}$  site symmetry) have structures with crystallographically imposed staggered conformations (Berger, Auner, & Bolte, 2014). The crystal structures of  $\text{Cl}_3\text{CCCl}_3$  in numerous polymorphs all crystallize with inversion site symmetries (Negrier, Tamarit, Barrio, & Mondieig, 2013; Sasada & Atoji, 1953).  $\text{Br}_3\text{CCBr}_3$  crystallizes staggered with  $m$  site symmetry both at RT (Mandel & Donohue, 1972) and at 100 K (refcode: HEXBME); a recent study reports co-crystals of  $\text{Br}_3\text{CCBr}_3$  with organometallic ruthenium complexes and here the molecules are found to be approximately staggered *without* crystallographic site symmetry in one case and in another to crystallize with  $\bar{1}$  site symmetry (refcodes: FALYOI, FALYOI01) (Fuller et al., 2012). Consistent with the very high barrier energies for conformational changes in  $\text{Br}_3\text{CCBr}_3$ , the geometry in the former structure has a largest BrCCBr torsion angle of  $179.4(4)^\circ$ , showing that it is effectively staggered even in the absence of lattice-imposed symmetry. The contrast with  $[\text{Ga}_2\text{Br}_6]^{2-}$ , which can adopt a wide range of conformations from eclipsed to staggered in different lattices, is dramatic.

### 3. Conclusions

Although it has been recognized since the discovery of the solid-state structures of  $\text{Li}_2[\text{Ga}_2\text{Br}_6]$  and  $\text{Ga}_2[\text{Ga}_2\text{Br}_6]$  that the barrier to Ga-Ga bond rotation in hexabromodigallate is likely to be small (Hönle et al., 1986; Hönle & Simon, 1986), no further investigation of this phenomenon appears to have been published. We have corrected the crystal structure of the phosphonium salt of this anion,  $[\text{Ph}_3\text{PH}]_2[\text{Ga}_2\text{Br}_6]$ , and demonstrated that here two out of three digallate anions have a distinctly intermediate conformation (smallest dihedral angle of  $36.91(1)^\circ$ ). Quantum calculations using standard DFT methods with large basis sets show that the barrier to rotation in the free, gas-phase anions is small, 4.3 and 5.1  $\text{kJ mol}^{-1}$  for the hexachloro- and hexabromodigallates, respectively. In this regard, the hexahalodigallates (Cl, Br, I) are shown to be good heavy main-group analogues to ethane. Whereas in a dicarbon molecule, replacing H with such halogens radically increases their conformational barrier energies, in the digallates the naturally large size of gallium is very well matched to the size of these halogen atoms and consequently have very low barriers for rotation. It is almost certain that similar ordered structures with different conformations pertain in the structures of  $[\text{Ph}_3\text{PH}]_2[\text{Ga}_2\text{X}_6]$  ( $\text{X} = \text{Cl}, \text{I}$ ) (Khan et al., 1986). The solid phases  $\text{LiGaCl}_3$  and  $\text{LiGaI}_3$  show eclipsed geometry for Cl and staggered for I (Hönle, Miller, & Simon, 1988).

## 4. Experimental Section

### 4.1. Synthesis

A 100-mL electrolysis cell equipped with a gallium metal anode and a platinum wire cathode was flushed with dry  $\text{N}_2$  gas, charged with 30 mL of acetonitrile, 0.50 g (1.5 mmol)  $\text{Ph}_3\text{P}$ , 2.0 mL (180 mmol) c. hydrobromic acid and cooled in an ice bath. A KEPCO ABC40 d.c. power supply and a Keithly 160B multimeter were used to maintain a steady-state current of 50 mA for the duration of the synthesis (~1.5 h). Yield: 0.20 g (0.23 mmol, 32% based on mass of gallium consumed) of colourless blocks (current efficiency =  $0.53\text{ mol F}^{-1}$ ). MP  $159.7\text{--}161.9^\circ\text{C}$  (lit.  $160\text{--}162^\circ\text{C}$ , Taylor & Tuck, 1983).

### 4.2. Crystal structure

Single crystals of  $\text{C}_{36}\text{H}_{32}\text{Br}_6\text{Ga}_2\text{P}_2$  precipitated during electrochemical synthesis. A suitable crystal was selected and mounted using a fine glass capillary in frozen Paratone oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at 173(2) K during data collection. Using Olex2 (Dolomanov, Bourhis, Gildea, Howard, & Puschmann, 2009), the structure was solved with the ShelXT (Sheldrick, 2015a) structure solution programme using “intrinsic phasing” and refined with the ShelXL (Sheldrick, 2015b) refinement package using least squares minimization. Hydrogen atoms on the phenyl rings

were treated as riding (C–H = 0.95 Å) with  $U_{\text{iso}} = 1.2 U$  of attached atom. The H atoms on P were restrained to a bond distance of 1.32 (2) Å and also have  $U_{\text{iso}} = 1.2 U$  of P atoms. Restraining these distances was necessary for a stable refinement. Crystal Data for  $\text{C}_{36}\text{H}_{32}\text{Br}_6\text{Ga}_2\text{P}_2$  ( $M = 1145.45$  g/mol): trigonal, space group  $P\bar{3}$  (No. 147),  $a = 13.9660$  (5) Å,  $c = 17.6075$  (7) Å,  $V = 2,974.2$  (2) Å<sup>3</sup>,  $Z = 3$ ,  $T = 173$  (2) K,  $\mu(\text{MoK}\alpha) = 7.510$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.919$  g/cm<sup>3</sup>, 37,168 reflections measured ( $3.368^\circ \leq 2\theta \leq 58.446^\circ$ ), 5,152 unique ( $R_{\text{int}} = 0.0246$ ,  $R_{\text{sigma}} = 0.0175$ ) which were used in all calculations. The final  $R_1$  was 0.0225 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.0510 (all data). Several different crystals were investigated; some data sets displayed rather large residual electron density peaks approximately half-way between a Ga and a P atom along the 3 and  $\bar{3}$ -axes. The reported structure is the one that was least affected by this phenomenon; no satisfactory twin-law could be found for these features. Structure illustrations as well as geometric and symmetry analyses were undertaken using Mercury release 3.9 (Macrae et al., 2006). CCDC 1515022 contains the data deposition for this crystal structure. These data can be obtained, free of charge, via <http://www.ccdc.cam.ac.uk/products/csd/request/> (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: 44-1223-336033 or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk))).

### 4.3. Computation

DFT calculations were undertaken at the B3LYP/6–31G(fd,) and B3LYP/6–311+G(fd,) levels of theory using Gaussian W03 (Frisch et al., 2004). These methods have been used in closely related systems and verified against experimental data for rotational barriers (Mo & Gao, 2007). The geometry of the non-centrosymmetric  $[\text{Ga}_2\text{Br}_6]^{2-}$  ion from the crystal structure was used as a starting point. Using either the smaller or larger basis sets, this geometry was found to be unstable towards the staggered conformation. Thereafter, the geometry was calculated at a series of fixed Br–Ga–Ga–Br torsion angles with full relaxation of all other variables. The torsions were stepped from 63° in 36 10-degree steps. With the smaller basis set, a metastable eclipsed form was detected with small local minima, but these disappear at the basis set limit. In no case was an intermediate conformation found to be stable. The chloro analogues were constructed from the original bromo anion by applying standard Ga–Cl single bond distances and then optimizing the same way as for the bromo species.

### Funding

The diffractometer was funded by the Natural Sciences and Engineering Research Council of Canada and by the University of Lethbridge.

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### Citation information

Cite this article as: Crystal structure of bis(triphenylphosphonium) hexabromodigallate(II) in the correct space group: Conformational complexity in a heteroethane, Olivia N.J.M. Marasco, Sydney K. Wolny, Jackson P. Knott, Daniel Stuart, Tracey L. Roemmele & René T. Boéré, *Cogent Chemistry* (2016), 2: 1273065.

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