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## Diethylgallium Diphenylphosphinate

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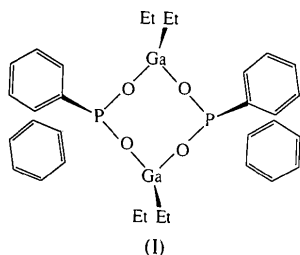
### Abstract

The title compound, bis( $\mu$ -diphenylphosphinato-*O*:*O'*)-bis(diethylgallium), [Ga<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>(C<sub>12</sub>H<sub>10</sub>O<sub>2</sub>P)<sub>2</sub>], contains discrete centrosymmetric molecules, each of which contains a puckered eight-membered (Ga—O—P—O)<sub>2</sub> ring. There are two crystallographically distinct molecules in the unit cell. The Ga—O bond distances range from 1.936 (2) to 1.946 (2) Å, while the P—O distances range from 1.513 (2) to 1.525 (2) Å.

### Comment

The title compound, (I), is of interest as a model compound for gallophosphate molecular sieves such as cloverite (Estermann, McCusker, Baerlocher, Merrouche & Kessler, 1991). Only a small amount of work has been carried out in this area and few compounds have been characterized fully. Coates & Mukherjee (1964) prepared the corresponding methyl derivative, [GaMe<sub>2</sub>(O<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>], and proposed a dimeric structure on the basis of IR and solution molecular-weight measurements.

The crystal structure of the title compound is found to contain discrete centrosymmetric molecules and the



asymmetric unit comprises two crystallographically independent half molecules. The structure of one of the molecules of [Et<sub>2</sub>Ga(O<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] is shown in Fig. 1. The molecules possess crystallographically imposed  $\bar{1}$  symmetry and contain a puckered eight-membered ring in which the four O atoms are, therefore, coplanar. In each ring, the four O atoms and two P atoms are close to being coplanar, with the two Ga atoms displaced out of this plane; displacements from the plane of the four O atoms are 0.044 (1) for P1 and 1.113 (1) Å for Ga1 of molecule 1, and -0.206 (1) for P2 and 0.941 (1) Å for Ga2 of molecule 2.

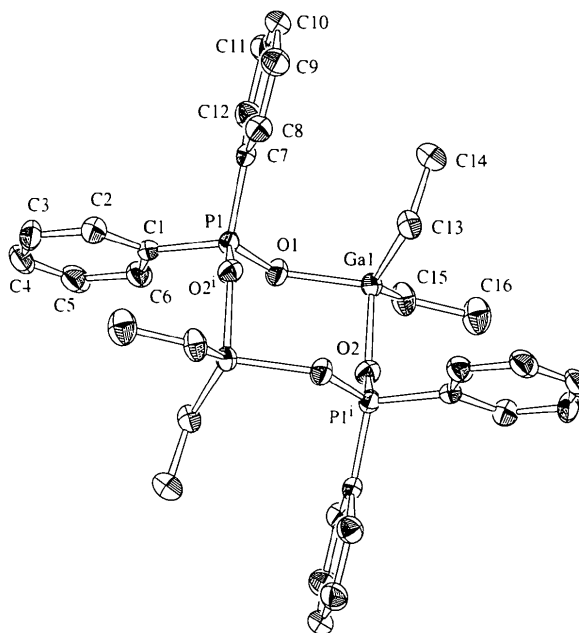


Fig. 1. The molecular structure of [Et<sub>2</sub>Ga(O<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] (molecule 1; molecule 2 is very similar) showing the atom-labelling scheme, with displacement ellipsoids drawn at the 50% probability level. H atoms are excluded for clarity. [Symmetry code: (i)  $-x + 1, -y - 1, -z$ .]

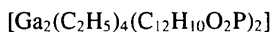
The geometry at the Ga and P atoms is approximately tetrahedral. The Ga—O bond distances are all very similar [1.936 (2)–1.946 (2) Å], as are the P—O bond distances [1.513 (2)–1.525 (2) Å]. The P—O—Ga angles are in the range 129.70 (13)–141.79 (14)°. The Ga—C distances [1.960 (3)–1.967 (3) Å] are within the expected range (Hahn, Schneider & Reier, 1990). Cryoscopic molecular-weight measurements in benzene (r.m.m. 705±25) established that the dimeric species persists in solution.

The compound shows the same cyclic structure as [Me<sub>2</sub>Ga(O<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>], where a similar deviation from planarity was observed (Hahn, Schneider & Reier, 1990). A similar ring system has been found in aluminium phosphinate compounds such as [Me<sub>2</sub>Al(O<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] (Corker, Browning & Webster, 1996), but in this case the eight-membered ring was found to be nearly planar.

## Experimental

Working under argon, the title compound was prepared by slowly adding GaEt<sub>3</sub> (3.4 mmol) dissolved in toluene to a cold (210 K) suspension of diphenylphosphinic acid (3.4 mmol) in toluene. The solution was allowed to warm slowly to room temperature and after stirring for 6 h, a clear solution had formed. Removal of the volatiles gave the required product in high yield and colourless crystals were obtained from toluene. The crystal was mounted in oil on a glass fibre for the low-temperature X-ray examination.

### Crystal data



$M_r = 690.02$

Triclinic

$P\bar{1}$

$a = 10.995(2) \text{ \AA}$

$b = 14.837(3) \text{ \AA}$

$c = 10.316(2) \text{ \AA}$

$\alpha = 102.63(2)^\circ$

$\beta = 96.95(2)^\circ$

$\gamma = 83.16(2)^\circ$

$V = 1622.6(6) \text{ \AA}^3$

$Z = 2$

$D_x = 1.412 \text{ Mg m}^{-3}$

$D_m$  not measured

### Data collection

Rigaku AFC-7S diffractometer

$\omega/2\theta$  scans

Absorption correction:

$\psi$  scan (North, Phillips & Mathews, 1968)

$T_{\min} = 0.74$ ,  $T_{\max} = 1.00$

6027 measured reflections

5701 independent reflections

4596 observed reflections

$[I > 2\sigma(I)]$

### Refinement

Refinement on  $F^2$

$R(F) = 0.0308$

$wR(F^2) = 0.0894$

$S = 1.020$

5701 reflections

361 parameters

H-atom parameters not refined

$w = 1/[\sigma^2(F_o^2) + (0.048P)^2 + 1.28P]$

where  $P = (F_o^2 + 2F_c^2)/3$

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{eq}}$
Ga1	0.58904 (3)	-0.48903 (2)	0.21046 (3)	0.02206 (10)
Ga2	0.91002 (3)	0.12414 (2)	0.40344 (3)	0.02151 (10)
P1	0.62632 (7)	-0.39985 (5)	-0.02988 (7)	0.0218 (2)

P2	0.89380 (7)	0.05315 (5)	0.67815 (7)	0.0216 (2)
O1	0.6693 (2)	-0.46518 (14)	0.0654 (2)	0.0272 (4)
O2	0.5008 (2)	-0.58984 (14)	0.1039 (2)	0.0270 (4)
O3	0.8498 (2)	0.08904 (15)	0.5524 (2)	0.0309 (5)
O4	0.9806 (2)	0.00205 (13)	0.3184 (2)	0.0256 (4)
C1	0.7401 (3)	-0.4173 (2)	-0.1462 (3)	0.0232 (6)
C2	0.7203 (3)	-0.3703 (2)	-0.2512 (3)	0.0321 (7)
C3	0.8073 (3)	-0.3821 (2)	-0.3419 (3)	0.0380 (8)
C4	0.9138 (3)	-0.4398 (2)	-0.3273 (3)	0.0402 (8)
C5	0.9352 (3)	-0.4865 (2)	-0.2238 (3)	0.0376 (8)
C6	0.8480 (3)	-0.4750 (2)	-0.1319 (3)	0.0307 (7)
C7	0.6238 (3)	-0.2818 (2)	0.0609 (3)	0.0224 (6)
C8	0.5172 (3)	-0.2213 (2)	0.0566 (3)	0.0291 (7)
C9	0.5145 (3)	-0.1313 (2)	0.1330 (3)	0.0351 (7)
C10	0.6190 (3)	-0.1018 (2)	0.2117 (3)	0.0342 (7)
C11	0.7261 (3)	-0.1606 (2)	0.2157 (3)	0.0351 (7)
C12	0.7287 (3)	-0.2506 (2)	0.1399 (3)	0.0305 (7)
C13	0.4671 (3)	-0.3846 (2)	0.2705 (3)	0.0299 (7)
C14	0.5163 (4)	-0.3077 (2)	0.3819 (4)	0.0446 (9)
C15	0.7171 (3)	-0.5482 (2)	0.3224 (3)	0.0324 (7)
C16	0.6643 (4)	-0.5792 (3)	0.4331 (4)	0.0442 (9)
C17	0.9004 (3)	0.1483 (2)	0.8198 (3)	0.0233 (6)
C18	0.8052 (3)	0.2192 (2)	0.8329 (3)	0.0327 (7)
C19	0.8086 (3)	0.2919 (2)	0.9431 (4)	0.0376 (8)
C20	0.9082 (3)	0.2945 (2)	1.0393 (3)	0.0386 (8)
C21	1.0032 (3)	0.2255 (3)	1.0268 (3)	0.0397 (8)
C22	0.9999 (3)	0.1511 (2)	0.9175 (3)	0.0302 (7)
C23	0.7766 (3)	-0.0155 (2)	0.7010 (3)	0.0234 (6)
C24	0.7841 (3)	-0.0501 (2)	0.8178 (3)	0.0283 (6)
C25	0.6958 (3)	-0.1037 (2)	0.8368 (4)	0.0364 (7)
C26	0.5994 (3)	-0.1240 (2)	0.7383 (4)	0.0381 (8)
C27	0.5909 (3)	-0.0904 (2)	0.6227 (3)	0.0377 (8)
C28	0.6792 (3)	-0.0358 (2)	0.6041 (3)	0.0308 (7)
C29	1.0457 (3)	0.2018 (2)	0.4721 (3)	0.0370 (8)
C30	1.0115 (3)	0.2912 (2)	0.5703 (4)	0.0436 (9)
C31	0.7583 (3)	0.1488 (2)	0.2897 (3)	0.0379 (8)
C32	0.7559 (4)	0.0986 (3)	0.1468 (3)	0.0456 (9)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Ga1—O1	1.941 (2)	P1—O1	1.525 (2)
Ga1—O2	1.938 (2)	P1—O2'	1.517 (2)
Ga1—C13	1.967 (3)	P1—C1	1.795 (3)
Ga1—C15	1.960 (3)	P1—C7	1.795 (3)
Ga2—O3	1.936 (2)	P2—O3	1.513 (2)
Ga2—O4	1.946 (2)	P2—O4''	1.520 (2)
Ga2—C29	1.963 (3)	P2—C17	1.798 (3)
Ga2—C31	1.965 (3)	P2—C23	1.802 (3)
O1—Ga1—O2	96.14 (9)	O1—P1—C7	109.57 (12)
O1—Ga1—C13	110.00 (11)	C1—P1—C7	107.75 (13)
O1—Ga1—C15	106.37 (11)	O3—P2—O4''	116.70 (12)
O2—Ga1—C13	107.85 (11)	O3—P2—C17	109.96 (13)
O2—Ga1—C15	104.99 (12)	O4''—P2—C17	106.41 (13)
C13—Ga1—C15	127.06 (13)	O3—P2—C23	106.01 (13)
O3—Ga2—O4	98.08 (9)	O4''—P2—C23	110.59 (12)
O3—Ga2—C29	108.59 (12)	C17—P2—C23	106.80 (13)
O4—Ga2—C29	107.89 (11)	P1—O1—Ga1	129.70 (13)
O3—Ga2—C31	102.96 (13)	P1'—O2—Ga1	136.39 (13)
O4—Ga2—C31	105.07 (12)	P2—O3—Ga2	141.79 (14)
C29—Ga2—C31	129.8 (2)	P2''—O4—Ga2	136.61 (13)
O2'—P1—O1	116.44 (12)	C14—C13—Ga1	115.0 (2)
O2'—P1—C1	110.26 (13)	C16—C15—Ga1	111.9 (2)
O1—P1—C1	106.45 (13)	C30—C29—Ga2	114.9 (2)
O2'—P1—C7	106.10 (13)	C32—C31—Ga2	115.6 (2)

Symmetry codes: (i)  $1 - x, -1 - y, -z$ ; (ii)  $2 - x, -y, 1 - z$ .

H atoms were placed in observed positions with a fixed displacement parameter and not refined.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1040). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Iodotris(triphenylphosphine)silver(I), [Ag(PPh<sub>3</sub>)<sub>3</sub>I]

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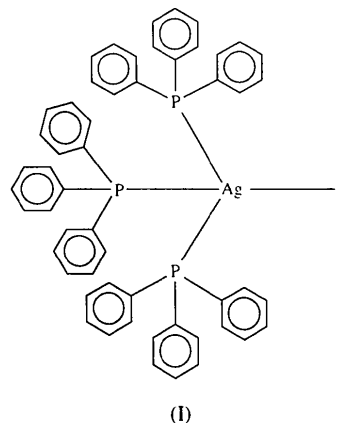
### Abstract

The geometry about the Ag atom in the title complex, [AgI(C<sub>18</sub>H<sub>15</sub>P)<sub>3</sub>], is distorted tetrahedral with the Ag—I bond length 2.8660 (11) Å and Ag—P distances 2.5335 (14), 2.5589 (12) and 2.6814 (12) Å. The P—Ag—P/I angles show large variations [104.54 (3)–116.10 (4)°] from the ideal tetrahedral value (109.45°).

These distortions, as well as those around the P atoms in the three triphenylphosphine ligands, may be attributed to several intramolecular (H···I and H···C/H) short contacts.

### Comment

A number of tris(triphenylphosphine)silver(I) derivatives of the type [Ag(PPh<sub>3</sub>)<sub>3</sub>X] have been characterized by X-ray crystallography: X = Cl (Cassel, 1981), X = Cl, Br or I (Englehardt, Healy, Patrick & White, 1987), X = I, BF<sub>4</sub> (Camalli & Caruso, 1987), and X = NO<sub>3</sub> (Barron *et al.*, 1986; Bruce & Duffy, 1986). All these complexes are molecular species, in each of which the Ag atom has distorted tetrahedral geometry. The nitrate derivative is monoclinic and isostructural with the room-temperature (RT) iodide structure reported by Englehardt *et al.* (1987), with the N atom of the bidentate nitrate group occupying almost the same position as the I atom. In the BF<sub>4</sub> complex there is one Ag—F interaction which is long [2.82 (1) Å], but it definitely indicates a bonding (albeit weak) interaction. The RT iodide structure reported



by Englehardt *et al.* (1987) is monoclinic with one long and two short Ag—P bonds [2.780 (3), 2.544 (2) and 2.573 (3) Å], while the structure reported by Camalli & Caruso (1987) is triclinic with the Ag—P bonds falling within a narrow range [2.572 (4)–2.616 (3) Å]. We undertook an X-ray study of the complex at 140 K (low temperature, LT) to obtain more accurate data and confirm the unusual variations in the reported molecular geometry parameters. The LT structure reported here (Fig. 1) is isostructural with the RT monoclinic form reported by Englehardt *et al.* (1987).

The Ag<sup>I</sup> centre is tetrahedral with one Ag—P bond [2.6814 (12) Å] much longer than the other two [2.5335 (14) and 2.5589 (12) Å]. These values follow the trend observed in the RT monoclinic structure (Englehardt *et al.*, 1987), but in the latter case the longest Ag—P bond is *ca* 0.10 Å longer than the corresponding value in our structure. The situation is somewhat dif-