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Palladium Complexes of 1,4,7-Trithiacyclodecane

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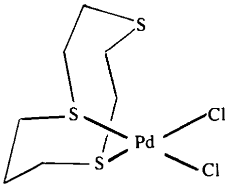
Abstract

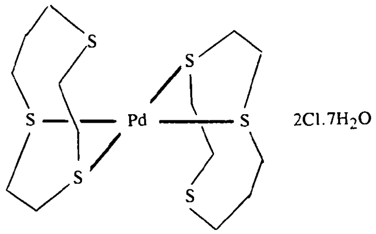
The 10S3 ligand in [Pd(10S3)Cl_2], dichloro(1,4,7-trithiacyclodecane)palladium(II), where 10S3 is 1,4,7-trithiacyclodecane, $C_7H_{14}S_3$, forms a six-membered chelate ring in which the average length of the two equatorial Pd—S bonds is 2.264 (2) Å and the weak axial Pd···S bond is 3.071 (2) Å. The same ligand in bis(1,4,7-trithiacyclodecane)palladium dichloride heptahydrate, [Pd$(10S3)_2$]Cl_2.7H_2O, forms two five-membered chelate rings, in which the average length of the four equatorial Pd—S bonds is 2.310 (1) Å and the length of the two weak axial Pd—S bonds is 3.051 (1) Å.

Comment

The molecular structure of [Pd(10S3)Cl_2] with the atomic labelling scheme is shown in Fig. 1 and that of the cation [Pd$(10S3)_2$]$^{2+}$ is shown in Fig. 2. In [Pd$(10S3)_2$]Cl_2.7H_2O, the Pd atom lies at a centre of symmetry, while the 10S3 ligand lies on a general position, generating another 10S3 ligand through $\bar{1}$ symmetry. One O atom from a water molecule and a chloride ion are disordered and are labelled as OCl.



[Pd(10S3)Cl_2]



[Pd$(10S3)_2$]Cl_2.7H_2O

The central Pd atom in [Pd(10S3)Cl_2] is surrounded by a distorted square-pyramidal array of two Cl atoms and three S atoms; the bond between the Pd atom and the axial S atom is weak [3.071 (2) Å] and is shorter than that in [Pd(9S3)Cl_2], where 9S3 is 1,4,7-trithiacyclononane [3.140 (2) Å; Blake, Holder, Roberts & Schröder, 1988]. The average length of the two equatorial Pd—S bonds is 2.264 (2) Å, close to that in [Pd(9S3)Cl_2] [2.256 (2) Å; Blake *et al.*, 1988].

The Pd atom in [Pd$(10S3)_2$]$^{2+}$ is in a distorted octahedral environment with four equatorial Pd—S bonds and two weak axial Pd···S interactions. The average length of the four equatorial Pd—S bonds [2.310 (1) Å] and that of the two weak axial Pd···S

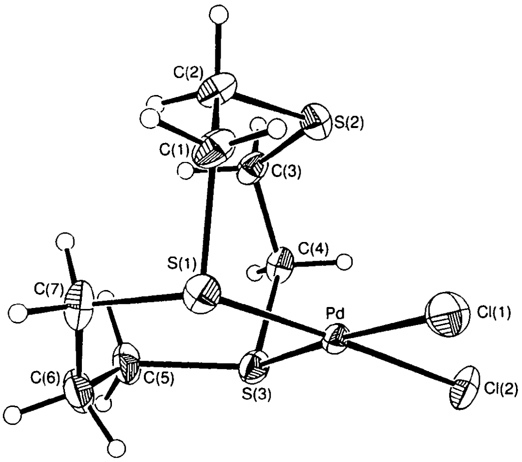


Fig. 1. The molecular structure of [Pd(10S3)Cl_2]. Displacement ellipsoids are shown at the 30% probability level.

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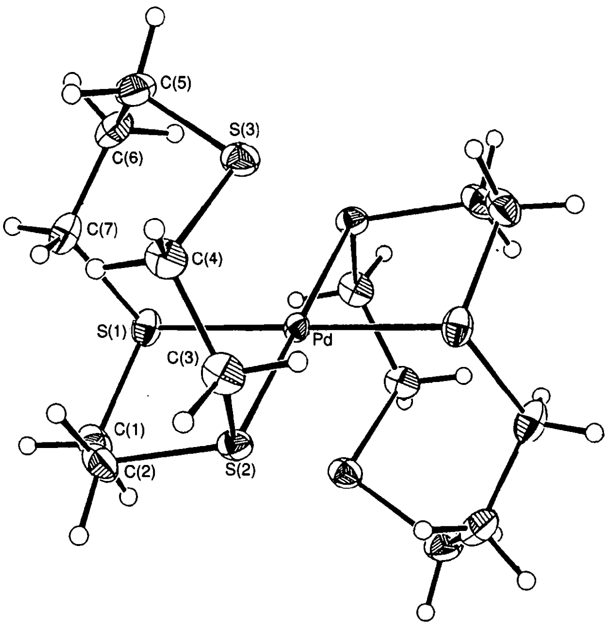

Fig. 2. The molecular structure of the $[Pd(10S3)_2]^{2+}$ cation. Displacement ellipsoids are shown at the 30% probability level.

interactions [3.051 (1) Å] are comparable with those in $[Pd(9S3)_2](PF_6)_2.H_2O$ [2.312 (2) and 3.005 (1) Å; Wieghardt, Küppers, Raabe & Krüger, 1986]. Data for three palladium complexes of 1,4,7-trithiacyclodecane (10S3) are given in Table 3. In $[Pd(10S3)_2](PF_6)_2.2CH_3NO_2$ (Grant, Carpenter, Setzer & VanDerveer, 1991) the mean equatorial Pd—S bond distances are significantly shorter than those in $[Pd(10S3)_2](PF_6)_2.2CH_3CN$ and $[Pd(10S3)_2]Cl_2.7H_2O$, which is likely to result from the spatial arrangement of the ligands. These bond distances are similar in $[Pd(10S3)_2](PF_6)_2.2CH_3CN$ (Chandrasekhar & McAuley, 1992) and $[Pd(10S3)_2]Cl_2{\cdot}7H_2O$, even though the anions and solvent molecules are different.

The stereochemical difference between $[Pd(10S3)Cl_2]$ and $[Pd(10S3)_2]Cl_2.7H_2O$ is that in the former the ligand forms a six-membered chelate ring whereas in the latter the ligands form two five-membered chelate rings. $[Pd(10S3)Cl_2]$ is formed as a labile intermediate during the synthesis of $[Pd(10S3)_2]Cl_2.7H_2O$.

Experimental

$[Pd(10S3)Cl_2]$ was prepared by refluxing $PdCl_2$ and 10S3 (1:1) in CH_3CN for 12 h. Red–brown crystals were obtained after one week by evaporating the solution in the air. On leaving the solution to stand for a further week, the red–brown crystals of $[Pd(10S3)Cl_2]$ redissolved and pale green crystals of $[Pd(10S3)_2]Cl_2.7H_2O$ were obtained. The densities D_m were measured by flotation.

$[Pd(10S3)Cl_2]$

Crystal data

$[PdCl_2(C_7H_{14}S_3)]$
$M_r = 371.7$
Orthorhombic
$P2_12_12_1$
$a = 7.565\ (1)$ Å
$b = 12.046\ (1)$ Å
$c = 13.701\ (1)$ Å
$V = 1248.4\ (2)$ Å^3
$Z = 4$
$D_x = 1.977$ Mg m^{-3}
$D_m = 1.958$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 18.5$–25°
$\mu = 2.34$ mm^{-1}
$T = 298$ K
Plate
0.20 × 0.15 × 0.10 mm
Red–brown

Data collection

Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.83$, $T_{max} = 1.00$
1283 measured reflections
1283 independent reflections

1091 observed reflections $[I \geq 2\sigma(I)]$
$\theta_{max} = 25°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 16$
3 standard reflections intensity decay: <2%

Refinement

$R = 0.026$
$wR = 0.026$
$S = 1.16$
1091 reflections
119 parameters
H atoms fixed at calculated positions with $U_H = U_{attached} + 0.01$ Å^2
$w = 1/[\sigma^2(F_o) + (0.002F_o)^2]$
$(\Delta/\sigma)_{max} = 0.007$
$\Delta\rho_{max} = 0.57$ e Å^{-3}
$\Delta\rho_{min} = -0.39$ e Å^{-3}

Extinction correction: Gaussian (Zachariasen, 1967)
Extinction coefficient: 0.34 (4)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

$[Pd(10S3)_2]Cl_2.7H_2O$

Crystal data

$[Pd(C_7H_{14}S_3)_2]Cl_2.7H_2O$
$M_r = 692.15$
Monoclinic
$C2/c$
$a = 18.117\ (1)$ Å
$b = 11.608\ (1)$ Å
$c = 13.611\ (1)$ Å
$\beta = 96.40\ (1)°$
$V = 2844.3\ (4)$ Å^3
$Z = 4$
$D_x = 1.616$ Mg m^{-3}
$D_m = 1.603$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 18.5$–25°
$\mu = 1.29$ mm^{-1}
$T = 298$ K
Plate
0.40 × 0.30 × 0.20 mm
Green

Data collection

Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.92$, $T_{max} = 1.00$
2503 measured reflections
2503 independent reflections

2013 observed reflections $[I \geq 2\sigma(I)]$
$\theta_{max} = 25°$
$h = -21 \rightarrow 21$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 16$
3 standard reflections intensity decay: <2%

Refinement

$R = 0.035$
$wR = 0.042$
$S = 2.66$
2013 reflections
140 parameters
H atoms fixed at calculated positions with $U_{\rm H} = U_{\rm attached} + 0.01$ Å^2
$w = 1/[\sigma^2(F_o) + (0.002F_c)^2]$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.61$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.70$ e Å^{-3}
Extinction correction: Gaussian (Zachariasen, 1967)
Extinction coefficient: 8.90 (4)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$B_{\rm eq} = (1/3)\Sigma_i\Sigma_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
[Pd(10S3)Cl$_2$]				
Pd	0.05887 (6)	0.16384 (4)	0.24350 (4)	2.37 (2)
Cl(1)	0.2134 (3)	0.1525 (2)	0.3908 (1)	4.18 (9)
Cl(2)	0.2972 (2)	0.2512 (2)	0.1675 (1)	3.85 (9)
S(1)	−0.1594 (3)	0.0708 (2)	0.3216 (1)	3.13 (8)
S(2)	−0.1767 (3)	0.3639 (2)	0.2924 (1)	3.35 (8)
S(3)	−0.0655 (2)	0.1793 (2)	0.0938 (1)	2.87 (7)
C(1)	−0.2563 (9)	0.1717 (7)	0.4028 (5)	3.5 (3)
C(2)	−0.3302 (9)	0.2763 (6)	0.3573 (5)	3.4 (3)
C(3)	−0.2627 (9)	0.3620 (6)	0.1698 (5)	2.8 (3)
C(4)	−0.1337 (9)	0.3228 (6)	0.0906 (5)	2.8 (3)
C(5)	−0.2728 (10)	0.1060 (7)	0.0772 (6)	3.8 (4)
C(6)	−0.2951 (10)	0.0059 (7)	0.1409 (6)	3.9 (4)
C(7)	−0.3455 (9)	0.0331 (6)	0.2448 (7)	3.9 (4)
[Pd(10S3)$_2$]Cl$_2$.7H$_2$O				
Pd	3/4	1/4	0	1.91 (2)
S(1)	0.87511 (7)	0.23925 (12)	0.05391 (9)	2.79 (5)
S(2)	0.77175 (7)	0.14434 (11)	−0.13782 (9)	2.53 (5)
S(3)	0.76428 (8)	0.45070 (11)	−0.14135 (10)	3.01 (6)
C(1)	0.9012 (3)	0.1152 (5)	−0.0158 (4)	3.5 (2)
C(2)	0.8716 (3)	0.1193 (5)	−0.1233 (4)	3.4 (2)
C(3)	0.7588 (3)	0.2408 (5)	−0.2426 (4)	3.1 (2)
C(4)	0.7975 (3)	0.3568 (5)	−0.2338 (4)	3.1 (2)
C(5)	0.8484 (3)	0.5219 (4)	−0.0869 (4)	3.7 (3)
C(6)	0.8862 (3)	0.4734 (5)	0.0085 (4)	3.7 (3)
C(7)	0.9233 (3)	0.3554 (5)	−0.0010 (4)	3.5 (2)
Cl	1	−0.3581 (2)	1/4	5.9 (1)
OCl(1)†	0.8055 (2)	−0.1626 (2)	−0.0185 (2)	5.5 (1)
O(2)	0	0.9699 (5)	3/4	5.0 (3)
O(3)	1	−0.3866 (6)	−1/4	7.2 (4)
O(4)	0.9302 (2)	−0.1999 (4)	−0.1500 (3)	5.4 (2)
O(5)	0.9321 (3)	−0.1469 (4)	0.1354 (4)	6.9 (3)

† Site occupancy is 50% O and 50% Cl.

Table 2. *Selected geometric parameters (Å, °)*

[Pd(10S3)Cl$_2$]			
Pd—Cl(1)	2.336 (2)	S(2)—C(3)	1.801 (7)
Pd—Cl(2)	2.333 (2)	S(3)—C(4)	1.805 (7)
Pd—S(1)	2.264 (2)	S(3)—C(5)	1.814 (7)
Pd···S(2)	3.071 (2)	C(1)—C(2)	1.51 (1)
Pd—S(3)	2.265 (2)	C(3)—C(4)	1.53 (1)
S(1)—C(1)	1.804 (8)	C(5)—C(6)	1.50 (1)
S(1)—C(7)	1.816 (8)	C(6)—C(7)	1.51 (1)
S(2)—C(2)	1.803 (8)		
[Pd(10S3)$_2$]Cl$_2$.7H$_2$O			
Pd—S(1)	2.307 (1)	S(2)—C(2)	1.821 (5)
Pd—S(1^{i})	2.307 (1)	S(2)—C(3)	1.807 (5)
Pd—S(2)	2.312 (1)	S(3)—C(4)	1.817 (5)
Pd—S(2^{i})	2.312 (1)	S(3)—C(5)	1.817 (6)
Pd···S(3)	3.051 (1)	C(1)—C(2)	1.503 (8)
Pd···S(3^{i})	3.051 (1)	C(3)—C(4)	1.517 (8)
S(1)—C(1)	1.815 (6)	C(5)—C(6)	1.509 (8)
S(1)—C(7)	1.812 (5)	C(6)—C(7)	1.538 (8)
[Pd(10S3)Cl$_2$]			
Cl(1)—Pd—Cl(2)	91.44 (7)	Pd···S(2)—C(2)	91.3 (2)
Cl(1)—Pd—S(1)	85.86 (8)	Pd···S(2)—C(3)	89.8 (2)
Cl(1)—Pd···S(2)	98.51 (6)	C(2)—S(2)—C(3)	102.7 (3)
Cl(1)—Pd—S(3)	174.41 (7)	Pd—S(3)—C(4)	102.7 (2)
Cl(2)—Pd—S(1)	176.15 (7)	Pd—S(3)—C(5)	115.6 (3)
Cl(2)—Pd···S(2)	101.06 (7)	C(4)—S(3)—C(5)	102.5 (3)
Cl(2)—Pd—S(3)	83.10 (7)	S(1)—C(1)—C(2)	117.2 (5)
S(1)—Pd···S(2)	82.07 (6)	S(2)—C(2)—C(1)	116.9 (5)
S(1)—Pd—S(3)	99.54 (7)	S(2)—C(3)—C(4)	115.7 (5)
S(2)···Pd—S(3)	83.78 (6)	S(3)—C(4)—C(3)	117.3 (5)
Pd—S(1)—C(1)	104.7 (3)	S(3)—C(5)—C(6)	114.6 (5)
Pd—S(1)—C(7)	114.5 (3)	C(5)—C(6)—C(7)	113.8 (7)
C(1)—S(1)—C(7)	102.2 (4)	S(1)—C(7)—C(6)	113.9 (5)
[Pd(10S3)$_2$]Cl$_2$.7H$_2$O			
S(1)—Pd—S(1^{i})	180	Pd—S(1)—C(7)	109.3 (2)
S(1)—Pd—S(2)	88.80 (5)	C(1)—S(1)—C(7)	102.1 (3)
S(1)—Pd—S(2^{i})	91.20 (5)	Pd—S(2)—C(2)	104.7 (2)
S(1)—Pd···S(3)	95.31 (4)	Pd—S(2)—C(3)	107.0 (2)
S(1)—Pd···S(3^{i})	84.69 (4)	C(2)—S(2)—C(3)	103.0 (3)
S(1^{i})—Pd—S(2)	91.20 (4)	Pd···S(3)—C(4)	92.1 (2)
S(1^{i})—Pd—S(2^{i})	88.80 (5)	Pd···S(3)—C(5)	102.5 (2)
S(1^{i})—Pd···S(3)	84.69 (4)	C(4)—S(3)—C(5)	103.2 (3)
S(1^{i})—Pd···S(3^{i})	95.31 (4)	S(1)—C(1)—C(2)	113.5 (4)
S(2)—Pd—S(2^{i})	180	S(2)—C(2)—C(1)	110.7 (4)
S(2)—Pd···S(3)	81.91 (4)	S(2)—C(3)—C(4)	118.0 (3)
S(2)—Pd···S(3^{i})	98.09 (4)	S(3)—C(4)—C(3)	113.7 (3)
S(2^{i})—Pd···S(3)	98.09 (4)	S(3)—C(5)—C(6)	117.5 (4)
S(2^{i})—Pd···S(3^{i})	81.91 (4)	C(5)—C(6)—C(7)	114.9 (5)
S(3)···Pd···S(3^{i})	180	S(1)—C(7)—C(6)	113.1 (4)
Pd—S(1)—C(1)	100.4 (2)		

Symmetry code: (i) $\frac{3}{2} - x, \frac{1}{2} - y, -z$.

Table 3. *Mean Pd—S bond lengths (Å) for some bis(1,4,7-trithiacyclodecane)palladium complexes*

	Mean equatorial bond length	Mean axial bond length	Colour
[Pd(10S3)$_2$](PF$_6$)$_2$.2CH$_3$NO$_2$^{a}	2.27	3.11	Blue–green
[Pd(10S3)$_2$](PF$_6$)$_2$.2CH$_3$CN^{b}	2.329	3.034	Green
[Pd(10S3)$_2$]Cl$_2$.7H$_2$O^{c}	2.310	3.051	Green

References: (*a*) Grant, Carpenter, Setzer & VanDerveer (1991); (*b*) Chandrasekhar & McAuley (1992); (*c*) this work.

The structures were solved by the Patterson method and were refined by a least-squares method. All non-H atoms were refined with anisotropic displacement parameters. Data reduction and structure refinement were performed using *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: HL1041). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Diethylgallium Diphenylphosphinate

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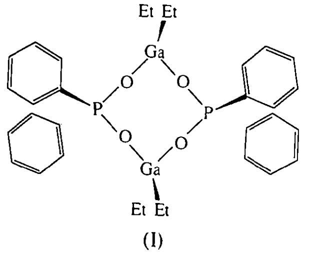
Abstract

The title compound, bis(μ-diphenylphosphinato-*O*:*O*′)-bis(diethylgallium), [$Ga_2(C_2H_5)_4(C_{12}H_{10}O_2P)_2$], contains discrete centrosymmetric molecules, each of which contains a puckered eight-membered (Ga—O—P—O)$_2$ 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, [$GaMe_2(O_2PPh_2)]_2$, 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 [$Et_2Ga(O_2PPh_2)]_2$ 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.



(I)

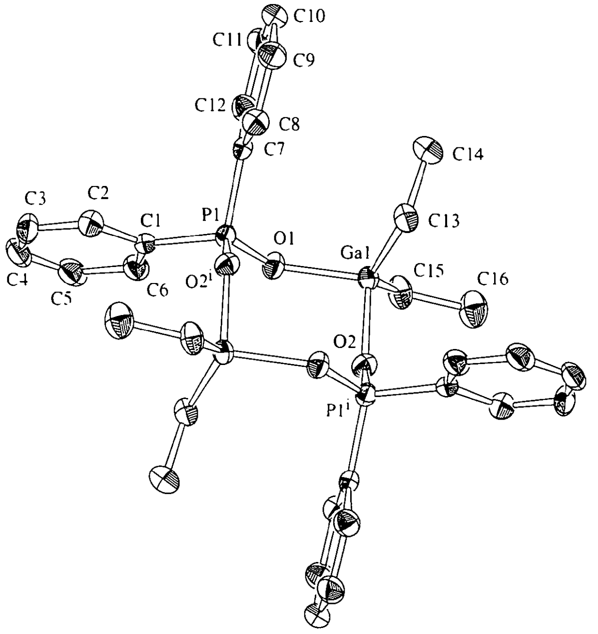


Fig. 1. The molecular structure of [$Et_2Ga(O_2PPh_2)]_2$ (molecule 1; molecule 2 is very similar) showing the atom-labelling scheme, with displacement ellipsoids drawn at the 50% probability level. H atoms are excluded for clarity. [Symmetry code: (i) $-x+1, -y-1, -z$.]

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 [$Me_2Ga(O_2PPh_2)]_2$, 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 [$Me_2Al(O_2PPh_2)]_2$ (Corker, Browning & Webster, 1996), but in this case the eight-membered ring was found to be nearly planar.