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Tetrachlorobis(hexamethylphosphoramide-*O*)digallium(II)(*Ga—Ga*)

Clifton E. F. Rickard,[a] Michael J. Taylor[a] and Melvin Kilner[b]

[a] *Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand, and* [b] *Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, England. E-mail: c.rickard@auckland.ac.nz*

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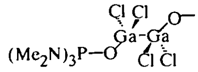
Abstract

The title compound, $[Ga_2Cl_4\{OP(C_2H_6N)_3\}]$, which lies about an inversion centre, has a Ga—Ga bond length of 2.392 (1) Å and a tetrahedral arrangement about each Ga atom. The ligands adopt a staggered conformation about the Ga—Ga bond. The Raman spectrum has a band at 254 cm^{-1} assigned to the Ga—Ga stretching mode.

Comment

While simple dihalides of gallium are mixed valence compounds, other compounds show an intense band in the Raman spectrum attributable to a Ga—Ga bond (Evans & Taylor, 1969). A number of complexes of the type $Ga_2Cl_4 \cdot 2L$ have been reported, along with the ionic species $Ga_2Cl_6^{2-}$ (Brown & Hall, 1973), which is constrained by space-group symmetry to have D_{3d} symmetry. The $Ga_2Cl_4 \cdot 2L$ species have no such constraint and are known both with the staggered conformation, Ga_2Cl_4·2(pyridine) (Beamish *et al.*, 1985), and in an almost eclipsed conformation, Ga_2Cl_4·2(dioxane) (Beamish *et al.*, 1979). We now report the structure of Ga_2Cl_4·2(hmpa), (I), for comparison with other known species (hmpa is hexamethylphosphoramide).



(I)

In Ga_2Cl_4·2(hmpa), the Ga—Ga bond lies on an inversion centre so that the staggered conformation is adopted, as in the pyridine complex, the trimethylamine complex (Pashkov *et al.*, 1996) and Ga_2Cl_4(4-mepy)$_2$ (4-mepy is 4-methylpyridine; Gordon *et al.*, 1997), which also have a crystallographically required staggered arrangement. The Ga—Ga bond length is 2.392 (1) Å. The other complexes have similar values: 2.406 (1) Å for L = dioxane, 2.403 (1) Å for L = pyridine, 2.421 Å for L = trimethylamine and 2.415 (2) Å for L = 4-methylpyridine. The corresponding Ga—Ga distance in $Ga_2Cl_6^{2-}$ is 2.390 (2) Å.

The Ga—O—P angle of 150.0 (3)° deviates considerably from linearity in contrast to $GaCl_3$·TPPO (TPPO is triphenylphosphine oxide; Burford *et al.*, 1990), where the arrangement is linear; however, in this case, the O-atom displacement parameter indicates that disorder is present, which would imply some degree of nonlinearity. The Ga—O distance is 1.881 (4) Å, which is similar to that found for $GaCl_3$·TPPO [1.818 (10) Å]. The torsion angle about the Ga—O bond is 176.9 (6)°, giving a staggered arrangement about this bond.

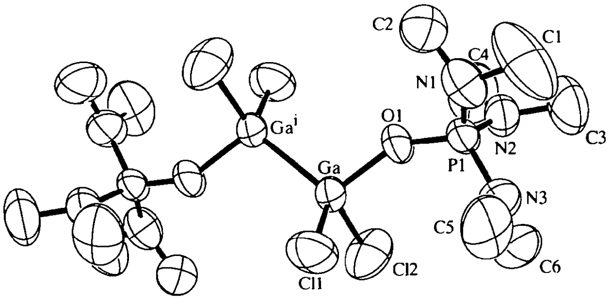


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. Only one of the two half-weighted C atoms (C2) is shown. H atoms have been omitted for clarity.

Experimental

The title compound was prepared directly from gallium metal used as the sacrificial anode of a cell in which the electrolyte was 10 ml of acetonitrile solution containing 0.5 ml of concentrated hydrochloric acid and 0.186 g of hexamethylphosphoramide. Electrolysis, with a current of 10–25 mA, took place for 5 h, during which time hydrogen was evolved from the platinum cathode and the gallium anode underwent a weight loss of 0.801 g. Tests for reducing power by removing small samples of the solution into aqueous $AgNO_3$ showed that a low-valent product was being formed. Following electrolysis, the solution was filtered and evaporated under vacuum to yield a colourless viscous liquid. The addition of methanol (1 ml) followed by diethyl ether (3 ml) led to the formation of colourless crystals. Analytical data: calculated for $C_{12}H_{36}Cl_4Ga_2N_6O_2P_2$: C 22.5, H 5.76, N 13.1%; found: C 22.3, H 5.69, N 12.9%. The far IR spectra of the crystals exhibited strong bands at 324 and 344 cm^{-1} attributable to Ga—Cl stretching vibrations, and the Raman spectrum contained an intense peak at 254 cm^{-1} assignable to a Ga—Ga bond-stretching mode. A representative crystal was selected for the crystallographic investigation reported here.

Crystal data

$[Ga_2Cl_4(C_6H_{18}N_3OP)_2]$
$M_r = 639.65$
Monoclinic
$P2_1/n$
$a = 9.060 (5)$ Å
$b = 11.4157 (12)$ Å
$c = 14.058 (4)$ Å
$\beta = 92.29 (3)°$
$V = 1452.8 (9)$ Å^3
$Z = 2$
$D_x = 1.462$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10–12°$
$\mu = 2.351$ mm^{-1}
$T = 293 (2)$ K
Rectangular prism
$0.32 \times 0.22 \times 0.20$ mm
Colourless

Data collection

Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.520$, $T_{max} = 0.651$
3357 measured reflections
2550 independent reflections

1312 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 24.97°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 13$
$l = -16 \rightarrow 16$
3 standard reflections every 200 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.117$
$S = 0.961$
2550 reflections
130 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0465P)^2 + 0.0517P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.324$ e Å^{-3}
$\Delta\rho_{min} = -0.300$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Ga—O1	1.881 (4)	P1—O1	1.477 (4)
Ga—Cl2	2.189 (2)	P1—N2	1.611 (6)
Ga—Cl1	2.200 (2)	P1—N1	1.620 (6)
Ga—Ga^i	2.3919 (14)	P1—N3	1.621 (6)
P1—O1—Ga	150.0 (3)		
Ga^i—Ga—O1—P1	176.9 (6)		

Symmetry code: (i) $-x, -y, 1 - z$.

The C atoms of the hexamethylphosphoramide groups show large displacement parameters indicative of disorder in these atoms. In one case, namely C2, the electron density could be resolved into two peaks and this atom was treated as two half-weighted atoms. In the remaining cases, the displacement parameters have been allowed to take up the disorder.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1994). Cell refinement: *CAD-4 Software*. Data reduction: local software. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *SHELXTL* (Siemens, 1994). Software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1238). Services for accessing these data are described at the back of the journal.

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trans-Chlorodifluorotris(pyridine-*N*)-osmium(III)

STEPHAN KOLF AND WILHELM PREETZ

Institut für Anorganische Chemie, Universität Kiel, Olshausenstraße 40, D-24098 Kiel, Germany. E-mail: kolf@ac.uni-kiel.de

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Abstract

The title compound, (*OC*-6-13)- or *trans*-$[OsClF_2(C_5H_5N)_3]$, is a novel fluorine-containing threefold