

A donor–acceptor adduct: sterically encumbered terphenyl dichloro[2,6-bis(2,4,6-triisopropylphenyl)-phenyl]dichloro(pyridine)gallium benzene hemisolvate

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Key indicators

Single-crystal X-ray study

$T = 90$ K

Mean $\sigma(\text{C}-\text{C}) = 0.011$ Å

R factor = 0.078

wR factor = 0.228

Data-to-parameter ratio = 16.1

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

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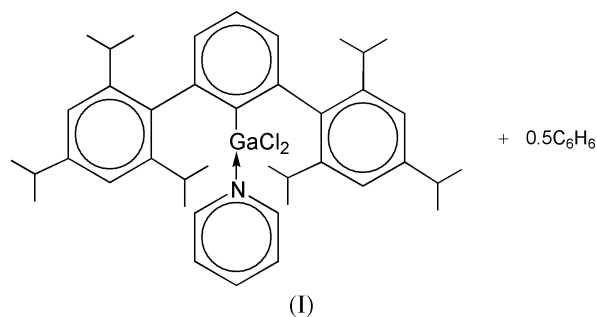
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The molecular structure of the benzene-solvated donor–acceptor complex dichloro[2,2'',4,4'',6,6''-hexaisopropyl-1,1':3',1''-terphenyl- C_{27}](pyridine)gallium benzene hemisolvate, henceforth known as 2,6-Trip₂-C₆H₃GaCl₂-pyridine benzene hemisolvate or (1) + 0.5 C₆H₆ (Trip = 2,4,6-triisopropylphenyl), [GaCl₂(C₃₆H₄₉)(C₅H₅N)]·0.5C₆H₆, has been determined. The asymmetric unit consists of four independent molecules of (1) and two benzene solvent molecules. The Ga–C, Ga–N and Ga–Cl bond lengths span the ranges 1.979 (7)–1.983 (2), 2.028 (6)–2.040 (7) and 2.179 (2)–2.212 (2) Å, respectively. All independent molecules of (1) have essentially the same geometry with slight differences in the orientation of the peripheral phenyl rings and isopropyl groups in the terphenyl moiety.

Comment

The addition of pyridine to 2,6-Trip₂-C₆H₃GaCl₂ (Trip = 2,4,6-triisopropylphenyl) in benzene results in the adduct 2,6-Trip₂-C₆H₃GaCl₂-pyridine, (1). (1) is an air-sensitive pale yellow high-melting solid that crystallizes in the monoclinic system with four crystallographically independent, chemically identical and geometrically similar adducts and two benzene solvent molecules in the asymmetric unit [descriptor (1) represents the full benzene-solvated title compound]. One of the independent molecules of the adduct is shown in Fig. 1.



The average Ga–C and Ga–Cl bonds [1.985 (7) and 2.195 (2) Å, respectively; Table 1] are slightly longer than analogous bonds in the base-free chloride 2,6-Trip₂-C₆H₃-GaCl₂ [Twamley & Power, 1999; 1.930 (8) Å, and 2.124 (3) and 2.113 (4) Å, respectively] obviously due to the electronic effect of the pyridine donation. The Ga–N distances in (1) [2.028 (6)–2.040 (7) Å] are in good agreement with the corresponding bonds in previously reported gallium chloride complexes that have coordination Ga–N bonds in chelate cycles [Ga–N 2.034 (8)–2.071 (2) Å; Al-Juaid *et al.*, 1999; Jutzi *et al.*, 1996; Isom *et al.*, 1995]. The torsion angles about

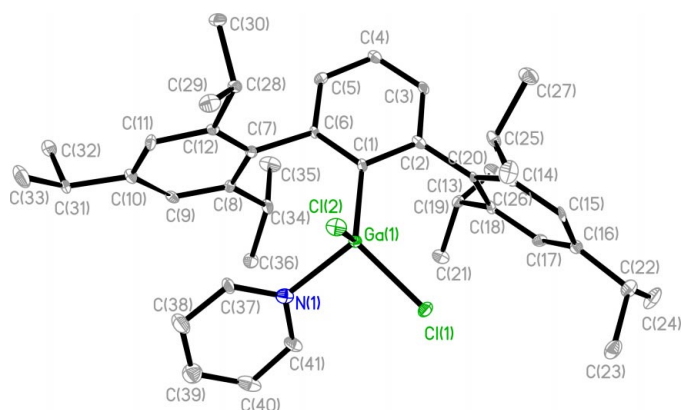


Figure 1

An ORTEP diagram of one of the independent molecules of (1) with 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

the four rotatable bonds in each of the independent molecules [Ga–N, Ga–C_{ipso}, two *ortho*-C–C (*ipso* pendant phenyl group); see Table 1] show that all four molecules have essentially similar geometry. Although these core torsion angles are similar, the pendant phenyl and isopropyl-group orientations are slightly different from molecule to molecule. This difference may be seen in Fig. 2, which shows the superposition of two molecules in the case of the the best and worst pairwise overlap (*i.e.* the Ga2/Ga1 and Ga3/Ga2 molecule pairs) of the central aromatic terphenyl core and the GaCl₂-pyridine moiety. This is also reflected in the weighted r.m.s. fit values as calculated by the OFIT procedure (Sheldrick, 1998*b*; Table 2), which performs the best possible fit of the similar molecular fragments.

The crystal packing (Fig. 3) in the structure of (1) features pairs of stacks of the adduct molecules running along the [010] direction with the GaCl₂-pyridine moieties facing each other within each pair of stacks. The benzene solvent molecules fill in the voids between the stack pairs. There are no specific intermolecular interactions between the molecules or the solvent.

Experimental

Dry pyridine (0.22 ml, 2.60 mmol) was added *via* syringe to a suspension of 2,6-Trip₂-C₆H₃GaCl₂ (Twamley & Power, 1999) in benzene (50 ml). The mixture was stirred overnight and then the solvent concentrated under reduced pressure to *ca* 10 ml. The suspension was warmed to redissolve precipitates and allowed to cool slowly to room temperature under an N₂ gas flow. The product crystallized after *ca* 10 min as pale yellow needles. Yield 1.21 g, 62%, m.p. 477–478 K. ¹H NMR (C₆D₆, 300 MHz): δ 1.20 [*d*, 12H, *o*-CH(CH₃)₂, ³J_{HH} = 6.9 Hz], 1.24 [*d*, 12H, *o*-CH(CH₃)₂, ³J_{HH} = 6.9 Hz], 1.35 [*d*, 12H, *p*-CH(CH₃)₂, ³J_{HH} = 6.6 Hz], 2.85 (*sept*, 3H, *o,p*-CH, ³J_{HH} = 6.9 Hz), 6.97 (*t*, 1H, *p*-C₆H₃, ³J_{HH} = 6.6 Hz), 7.07, (*d*, 2H, *m*-C₆H₃, ³J_{HH} = 7.35 Hz), 7.23 (*s*, 4H, *m*-Trip). ¹³C {¹H} NMR (C₆D₆, 75 MHz): δ 24.3, 24.5, 24.9, 31.6, 34.9, 121.1 (*m*-Trip), 126.4 (*p*-C₆H₃),

130.5 (*m*-C₆H₃), 135.1 (*o*-C₆H₃), 135.7 (*ipso* C), 140.8 (*i*-Trip), 146.6 (*o*-Trip), 148.9 (*p*-Trip).

Crystal data

[GaCl₂(C₃₆H₄₉)(C₅H₅N)]·0.5C₆H₆
M_r = 740.52
 Monoclinic, *P*2₁/*c*
a = 24.334 (2) Å
b = 20.954 (2) Å
c = 32.936 (3) Å
 β = 104.706 (2)°
V = 16244 (3) Å³
Z = 16

D_x = 1.211 Mg m⁻³
 Mo K α radiation
 Cell parameters from 6390 reflections
 θ = 2.4–30.9°
 μ = 0.84 mm⁻¹
T = 90 (2) K
 Needle, pale yellow
 0.52 × 0.25 × 0.07 mm

Data collection

Bruker SMART 1000 diffractometer
 ω scans
 Absorption correction: empirical (SADABS; Sheldrick, 1998*a*)
*T*_{min} = 0.670, *T*_{max} = 0.944
 163 360 measured reflections
 28 585 independent reflections
 13 485 reflections with *I* > 2 σ (*I*)

*R*_{int} = 0.137
 θ _{max} = 25.0°
h = –28 → 27
k = 0 → 24
l = 0 → 39
 50 frames remeasured at end of data collection
 intensity decay: none

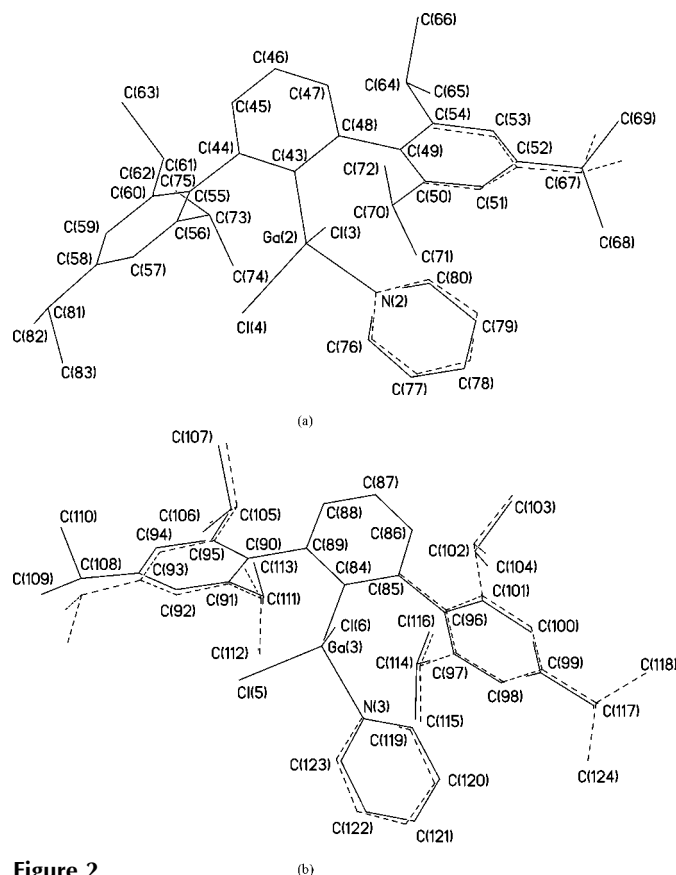


Figure 2

OFIT-generated superimposition diagram of (a) the best fit, Ga2 and Ga1 molecules and (b) the worst fit, Ga3 and Ga2 molecules. H atoms have been omitted. The numbering scheme is given for only the first molecule in each pair. Deviations from overlap are represented by dashed lines.

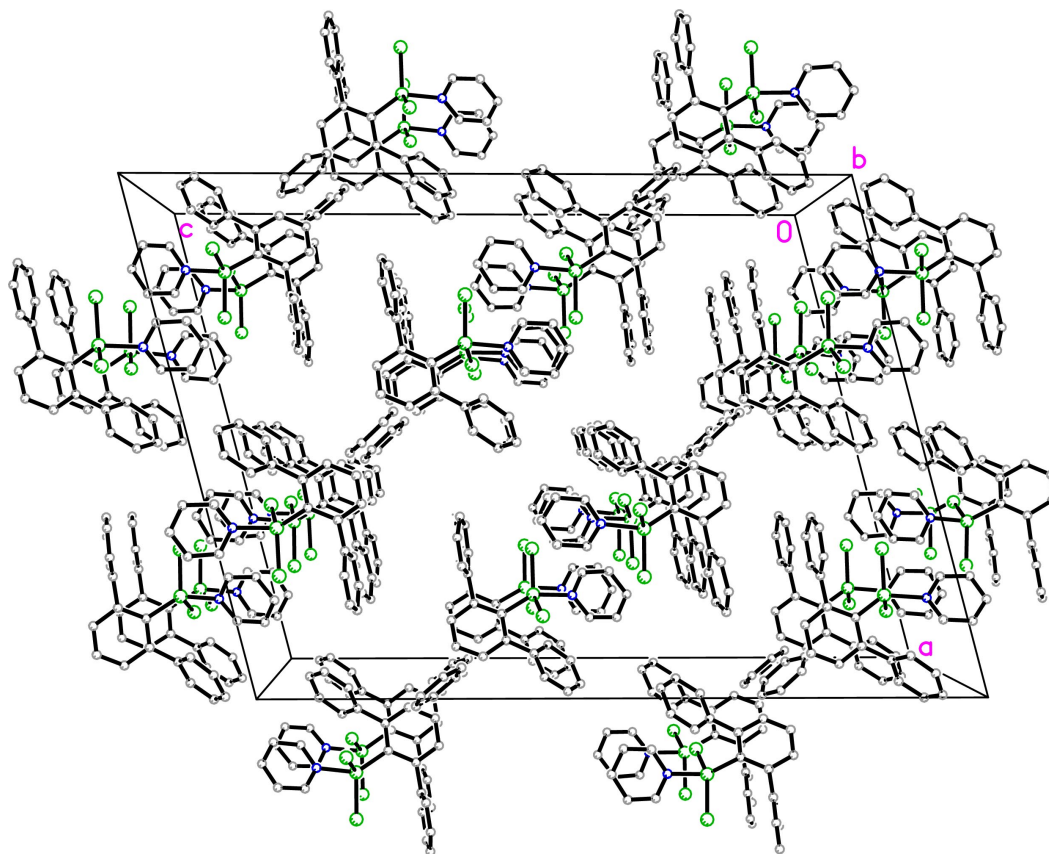


Figure 3
Packing diagram of (1) viewed down [010]. Isopropyl groups and H atoms have been omitted for clarity.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.078$
 $wR(F^2) = 0.228$
 $S = 1.13$
 28585 reflections
 1777 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0626P)^2 + 88.0236P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.02 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.38 \text{ e } \text{\AA}^{-3}$

| | | | |
|-----------------|------------|---------------------|-----------|
| C1—Ga1—N1—C37 | -77.2 (6) | C84—Ga3—N3—C119 | 81.3 (6) |
| N1—Ga1—C1—C2 | -149.6 (5) | N3—Ga3—C84—C89 | 150.9 (5) |
| C1—C2—C13—C14 | -89.7 (8) | C84—C85—C96—C97 | 83.9 (9) |
| C1—C6—C7—C8 | -83.8 (9) | C84—C89—C90—C95 | 94.2 (9) |
| C11—Ga1—C1—C2 | -29.6 (6) | C15—Ga3—C84—C89 | 30.2 (6) |
| C12—Ga1—C1—C2 | 97.6 (5) | C16—Ga3—C84—C89 | -96.7 (6) |
| C43—Ga2—N2—C80 | 83.7 (6) | C125—Ga4—N4—C161 | 82.2 (6) |
| N2—Ga2—C43—C44 | 147.1 (5) | N4—Ga4—C125—C126 | 150.2 (5) |
| C43—C48—C49—C50 | 81.2 (9) | C125—C126—C137—C142 | 96.4 (8) |
| C43—C44—C55—C60 | 90.7 (8) | C125—C130—C131—C132 | 78.2 (9) |
| C14—Ga2—C43—C44 | 27.7 (6) | C17—Ga4—C125—C126 | -95.6 (5) |
| C13—Ga2—C43—C44 | -99.7 (5) | C18—Ga4—C125—C126 | 30.4 (6) |

Table 1

Selected geometric parameters (\AA , $^\circ$).

| | | | |
|-------------|------------|--------------|------------|
| Ga1—C11 | 2.187 (2) | Ga3—C15 | 2.179 (2) |
| Ga1—C12 | 2.212 (2) | Ga3—C16 | 2.204 (2) |
| Ga1—N1 | 2.040 (7) | Ga3—N3 | 2.032 (6) |
| Ga1—C1 | 1.980 (7) | Ga3—C84 | 1.979 (7) |
| Ga2—C13 | 2.205 (2) | Ga4—C17 | 2.209 (2) |
| Ga2—C14 | 2.184 (2) | Ga4—C18 | 2.183 (2) |
| Ga2—N2 | 2.034 (6) | Ga4—N4 | 2.028 (6) |
| Ga2—C43 | 1.983 (7) | Ga4—C125 | 1.981 (6) |
| C1—Ga1—N1 | 120.1 (3) | C84—Ga3—N3 | 120.6 (3) |
| C1—Ga1—C11 | 120.7 (2) | C84—Ga3—C15 | 119.7 (2) |
| N1—Ga1—C11 | 96.65 (19) | N3—Ga3—C15 | 97.36 (18) |
| C1—Ga1—C12 | 111.3 (2) | C84—Ga3—C16 | 110.9 (2) |
| N1—Ga1—C12 | 97.5 (2) | N3—Ga3—C16 | 97.13 (18) |
| C11—Ga1—C12 | 107.40 (8) | C15—Ga3—C16 | 108.08 (9) |
| C43—Ga2—N2 | 119.9 (3) | C125—Ga4—N4 | 119.7 (3) |
| C43—Ga2—C14 | 120.6 (2) | C125—Ga4—C18 | 121.2 (2) |
| N2—Ga2—C14 | 96.44 (19) | N4—Ga4—C18 | 96.52 (18) |
| C43—Ga2—C13 | 111.4 (2) | C125—Ga4—C17 | 110.4 (2) |
| N2—Ga2—C13 | 97.84 (18) | N4—Ga4—C17 | 99.28 (19) |
| C14—Ga2—C13 | 107.56 (8) | C18—Ga4—C17 | 106.90 (8) |

Table 2

Results of the pairwise superposition of independent adduct molecules performed by matching the terphenyl core aromatic unit (isopropyl groups omitted from fit) and the GaCl_2 :pyridine fragment using the OFIT procedure (Sheldrick, 1998b).

| First molecule ^a | Second molecule ^a | Inverted ^b | Weighted r.m.s. fit value (\AA) |
|-----------------------------|------------------------------|-----------------------|--------------------------------------------|
| Ga2 | Ga1 | y | 0.1004 |
| Ga3 | Ga1 | y | 0.1034 |
| Ga4 | Ga1 | y | 0.1254 |
| Ga3 | Ga2 | n | 0.1443 |
| Ga4 | Ga2 | n | 0.1284 |
| Ga4 | Ga3 | n | 0.1311 |

† Notes: (a) Molecules are identified by their Ga atoms. (b) Flag 'y' in this column means the atomic coordinates of the second molecule from the reference list were inverted before fitting, 'n' means that they were not.

There is a high positive residual density of $1.02 \text{ e } \text{\AA}^{-3}$ near the Ga4 center. Several of the C atoms (C16, C39, C48, C125, C125 and C133) were restrained during the refinement to approximate isotropic behaviour using the *ISOR SHELXTL* command.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 1998); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998*b*); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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