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# [$\mu$-(1,4-Dibenzylpiperazine)-*N*:*N'*]bis(trimethylindium) Dibenzene Solvate

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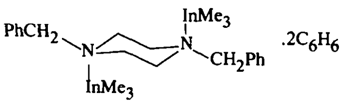
## Abstract

The X-ray crystal structure of the benzene solvated title compound, [In$_2$(C$_{18}$H$_{22}$N$_2$)(CH$_3$)$_6$].2C$_6$H$_6$, shows that the In atom has a four-coordinate distorted tetrahedral geometry, with an In—N bond length of 2.504 (4) Å. The C—In—C angles lie around 115° [114.1 (3)–116.5 (3)°] and the C—In—N angles range from 96.9 (2) to 110.7 (2)°. The piperazine ring is in a chair conformation. The two trimethylindium moieties are in a *trans* configuration and an axial conformation. The complex molecule is centrosymmetric.

## Comment

High purity trimethylindium has been used extensively in the preparation of compound semiconductor layers by metal organic chemical vapour deposition (MOCVD). The purity of trimethylindium is critical for the quality of the semiconductor material. Purification of trimethylindium by formation and then dissociation of an adduct is believed to be one of the best methods (Bradley, Chudzynska & Frigo, 1988; Bradley, Chudzynska, Factor *et al.*, 1988; Foster, Rushworth, Cole-Hamilton, Jones & Stagg, 1988). The present research is part of our efforts in search of better adducts for the purification of trimethylindium and related compounds and involves the structure determination of the dibenzene solvate of 1,4-bis(trimethylindium)-1,4-dibenzylpiperazine, (I).



(I)

The X-ray structure of (I) is presented in Fig. 1. Each N atom in the ligand coordinates to one trimethylindium moiety as expected. The In atom has a four-coordinate distorted tetrahedral geometry, with an In—N bond length of 2.504 (4) Å. The In—N bond length in the title compound is longer than the corresponding bond lengths found in Me$_3$InNHMe(CH$_2$)$_2$NHMeInMe$_3$ (2.369 and 2.393 Å) by about 5%, but comparable to that found in (2,2,6,6-tetramethylpiperidine)trimethylindium (2.502 Å; Bradley, Dawes, Frigo, Hursthouse & Hussain, 1987). The somewhat longer In—N bond length suggests repulsion between the methyl groups on the In atom and the methylene groups on the piperazine ring. The C(12)—In—N(1) bond angle is 110.7 (2)°, about 10% bigger than C(10)—In—N(1) [99.9 (2)°] and 14% bigger than C(11)—In—N(1) [96.9 (2)°]. These values suggest strong repulsion between the C(12) group and the methylene groups on the piperazine ring. This is in good agreement with the torsion angle C(8)—N(1)—In—C(12) of 25.7 (4)°.

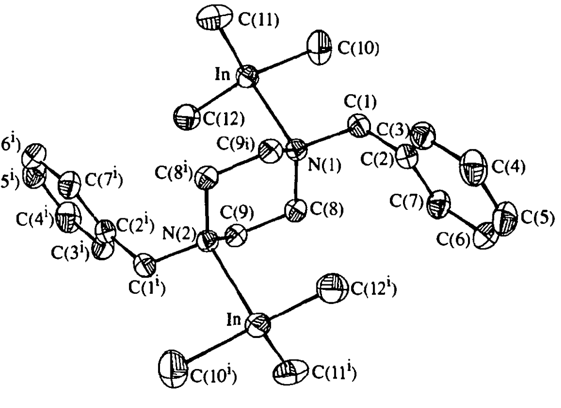


Fig 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

The piperazine ring is in a chair form. The two trimethylindium moieties are in a *trans* configuration and both are in axial positions. The trimethylindium group should be sterically bulkier than the benzyl group and so would be expected to adopt an equatorial position.

If we consider this further, however, we find that it is reasonable for the trimethylindium groups to take the axial conformation. It can be noted that the C(1)—N(1) and C(1$^{i}$)—N(2) bonds are much stronger than the In—N bonds [symmetry code: (i) $1-x$, $2-y$, $-z$]. The C(1) and C(1$^{i}$) atoms of the benzyl groups are closer to the N atoms than the In atoms in the trimethylindium moieties, therefore, a more repulsive force against the piperazine ring would be produced if the benzyl groups adopted axial positions.

The complex molecule is centrosymmetric. The long In—N distance indicates that bond strength or interaction between the In atoms and the N atoms of the piperazine ring is rather weak. This implies that 1,4-dibenzylpiperazine could be a good ligand for use in the purification of trimethylindium. Further research is underway in this laboratory.

## Experimental

All the manipulations were performed in a glove box under purified nitrogen. Solvents were heated under reflux with sodium benzophenone and distilled under nitrogen prior to use. 1,4-Dibenzylpiperazine was dissolved in a 2:1 benzene–petroleum ether (303–333 K) solution. A solution of trimethylindium in benzene was added dropwise with stirring. After stirring the mixture at 323 K for 2 h, most of the solvents were removed under vacuum and a white precipitate filtered off. A single crystal was obtained by recrystallization from benzene and was sealed in a glass capillary under nitrogen.

*Crystal data*

$[In_2(C_{18}H_{22}N_2)(CH_3)_6].2C_6H_6$
$M_r = 742.46$
Triclinic
$P\bar{1}$
$a = 9.543\,(4)$ Å
$b = 10.176\,(2)$ Å
$c = 11.340\,(3)$ Å
$\alpha = 84.56\,(2)^\circ$
$\beta = 113.62\,(3)^\circ$
$\gamma = 114.04\,(2)^\circ$
$V = 918.4\,(6)$ Å$^3$
$Z = 1$
$D_x = 1.34$ Mg m$^{-3}$
$D_m$ not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 20 reflections
$\theta = 13.35–21.20^\circ$
$\mu = 1.259$ mm$^{-1}$
$T = 296$ K
Prism
$1.0 \times 0.6 \times 0.6$ mm
Colourless

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (*TEXSAN*; Molecular Structure Corporation, 1987)
$T_{min} = 0.404$, $T_{max} = 0.470$
3443 measured reflections
3221 independent reflections
2669 reflections with $I > 3\sigma(I)$
$R_{int} = 0.0359$
$\theta_{max} = 25^\circ$
$h = 0 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -13 \rightarrow 13$
3 standard reflections
frequency: 300 min
intensity decay: 1.7%

*Refinement*

Refinement on $F$
$R = 0.052$
$wR = 0.063$
$S = 1.94$
2669 reflections
182 parameters
H atoms not refined
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.76$ e Å$^{-3}$
$\Delta\rho_{min} = -0.71$ e Å$^{-3}$
Extinction correction: Gaussian isotropic (Zachariasen, 1967)
Extinction coefficient: $5.0 \times 10^{-5}$
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

| | | | |
|---|---|---|---|
| In—C(11) | 2.161 (8) | N(1)—C(9$^{i}$) | 1.473 (6) |
| In—C(12) | 2.163 (7) | N(1)—C(8) | 1.481 (7) |
| In—C(10) | 2.189 (7) | N(1)—C(1) | 1.505 (6) |
| In—N(1) | 2.504 (4) | | |
| C(11)—In—C(12) | 116.5 (3) | C(9$^{i}$)—N(1)—In | 111.0 (3) |
| C(11)—In—C(10) | 115.8 (4) | C(8)—N(1)—C(1) | 110.6 (4) |
| C(11)—In—N(1) | 96.9 (2) | C(8)—N(1)—In | 115.8 (3) |
| C(12)—In—C(10) | 114.1 (3) | C(1)—N(1)—In | 100.8 (3) |
| C(12)—In—N(1) | 110.7 (2) | C(2)—C(1)—N(1) | 117.5 (4) |
| C(10)—In—N(1) | 99.9 (2) | N(1)—C(8)—C(9) | 111.3 (4) |
| C(9$^{i}$)—N(1)—C(8) | 107.8 (4) | N(1)—C(9$^{i}$)—C(8$^{i}$) | 111.7 (4) |
| C(9$^{i}$)—N(1)—C(I) | 110.7 (4) | | |

Symmetry code: (i) $1-x, 2-y, -z$.

The title structure was solved by the heavy-atom method (*DIRDIF*; Beurskens, 1984). H atoms were added geometrically. All calculations were performed using *TEXSAN* (Molecular Structure Corporation, 1987). *ORTEP*II (Johnson, 1976) was used to produce the figure and *CAD-4 Software* (Enraf–Nonius, 1989) was used for data collection and cell refinement.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: KH1102). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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