

A Six-coordinate Complex of Indium(III) Containing Trimethylindium Bonded to *N,N',N''*-Triisopropyl-1,3,5-triazacyclohexane

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$\text{Me}_3\text{In}(\text{Pr}^i\text{NCH}_2)_3$ has been shown by X-ray crystallographic analysis to be the first example of a six-coordinate indium(III) complex containing trimethylindium bonded to a terdentate nitrogen donor ligand; the In–N bonds [2.776(17) and 2.776(13) Å] are the longest In–N bonds measured so far.

There are many examples of trimethylindium acting as a one lone pair acceptor¹ but only rarely are adducts formed where two or more Lewis-base donor atoms are present per indium atom. Notable examples of this group are the adducts with bis(dimethylamino)methane² and with diazabicyclo[2.2.2]octane (DABCO)³, though only the DABCO adduct has been crystallographically characterized. We report here the structure of the trimethylindium adduct of *N,N',N''*-triisopropyl-1,3,5-triazacyclohexane, $\text{Me}_3\text{In}(\text{Pr}^i\text{NCH}_2)_3$ **1**, which shows trimethylindium accepting three lone pairs.

The adduct is air-sensitive and was handled under dry nitrogen during its synthesis and characterization. It was prepared by adding $(\text{Pr}^i\text{NCH}_2)_3$ (12 mmol) to a solution of Me_3In (12 mmol) in ether (30 ml). A small amount of white precipitate formed, which increased when the solution was cooled to -78°C . The supernatant liquid was concentrated *in vacuo* to give a crop of crystals suitable for analysis by X-ray crystallography.‡

The structure of **1** is shown in Fig. 1. The indium atom lies in the crystallographic mirror plane and above the six-membered triazane ring. The isopropyl groups are all in equatorial positions on the ring and the nitrogen atoms bonded to indium are all staggered with respect to the indium–methyl bonds. This is the first structurally characterized example of a triazane ring that forms bonds with all three nitrogen lone pairs: triazanes have only been found previously to donate one electron pair to a metal atom.⁴ The paucity of examples where trimethylindium accepts more than one lone pair may be due to either steric crowding around the indium by most ligands, or a weakening in adduct bond strength for any further electron-pair donation.

The structure of **1** has extensive disorder in the isopropyl groups of the triazane ring. The presence of a disordered phase was suggested by vapour-pressure measurements, which gave an entropy of sublimation about $24 \text{ J mol}^{-1} \text{ K}^{-1}$ lower than that predicted from interpolation of data for other adducts in the series $\text{Me}_3\text{In}(\text{RNCH}_2)_3$ (R = Me, Bu^t). Using

statistical thermodynamics ($S = k \ln W$), this corresponds to an approximate eighteenfold increase in arrangements compared with an ordered structure; with three isopropyl groups, this gives six arrangements per group. The disorder has been modelled on this basis, with an occupancy per site refined to match the relative peak intensities. Two of the predicted sites in the isopropyl group on N(2) are found to be unoccupied.

Interestingly, the angles between the indium–carbon bonds [$\text{C}(1)\text{--In}(1)\text{--C}(2) = 114.0(6)^\circ$ and $\text{C}(1)\text{--In}(1)\text{--C}(1') = 116.8(6)^\circ$] give a shallow InC_3 pyramid, which is typical for crystallographically characterized adducts where the trimethylindium has accepted only one electron pair. The indium–carbon bonds, however, show a slight elongation [$\text{In}(1)\text{--C}(1) = 2.223(14)$ and $\text{In}(1)\text{--C}(2) = 2.247(18)$ Å] relative to those found previously, *viz.* 2.147–2.186 Å. Whilst the errors make the differences statistically uncertain, the indium–nitrogen bond lengths are definitely the longest so far characterized. Previously the longest In–N bond known was 2.621(8) Å in the DABCO adduct, where the trimethylindium accepts two electron pairs. In the triazane adduct, where three lone pairs bond the adduct, the bond lengths are $\text{In}(1)\text{--N}(1) = 2.776(17)$ and two $\text{In}(1)\text{--N}(2) = 2.776(13)$ Å. This equality suggests that the interactions of the indium with each of the nitrogens are similar; their unprecedented long bond lengths suggest that each interaction is very much weaker than in normal two-electron adduct bonds. The N–In–N angles are also extremely acute [$\text{N}(1)\text{--In}(1)\text{--N}(2) = 48.8(3)^\circ$ and $\text{N}(2)\text{--In}(1)\text{--N}(2') = 48.5(5)^\circ$]. The distance between the methyl groups on trimethylindium and the nearest atoms of the ligand is greater in the triazane than the DABCO adduct. These nearest atoms are also sites of disorder (the ends of the isopropyl groups). This implies that no strong repulsion exists between the substituents of the ligand and those of the indium, else these sites would not be occupied at all. It can be concluded, therefore, that additional adduct bonds formed by trimethylindium are longer, hence weaker, owing to electronic rather than steric factors.

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‡ Satisfactory analyses were obtained. ¹H NMR (solvent C_7D_8) δ 3.38 (2H, s, CH_2), 2.80 (1H, septet, J 6.5 Hz, CHMe_2), 0.95 (6H, d, J 6.5 Hz, CHMe_2), and -0.03 (3H, s, InMe); IR (Nujol mull): ν/cm^{-1} 2950s, 2930s, 2755s, 2700sh, 2620sh, 2530sh, w, 1361s, 1331m, 1319m, 1302sh, 1219s, 1162s, 1120s, 1098s, 1001m, 940sh, 931m, 888w, 666s, 502m and 451s.

Crystal data for **1**: $\text{C}_{15}\text{H}_{36}\text{N}_3\text{In}$, $M = 373.291$, orthorhombic, space group $Pmn21$, $a = 12.861(1)$, $b = 9.890(1)$, $c = 7.823(1)$ Å, $U = 995.36(18)$ Å³, $Z = 2$, $D_c = 1.2455 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 2.83 \text{ cm}^{-1}$. Data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer with monochromated Mo-K α radiation. The data were corrected for Lorentz-polarization and absorption effects. Full-matrix least-squares refinement of 96 parameters gave $R = 0.0524$, $R_w = 0.0509$ for 988 unique reflections. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

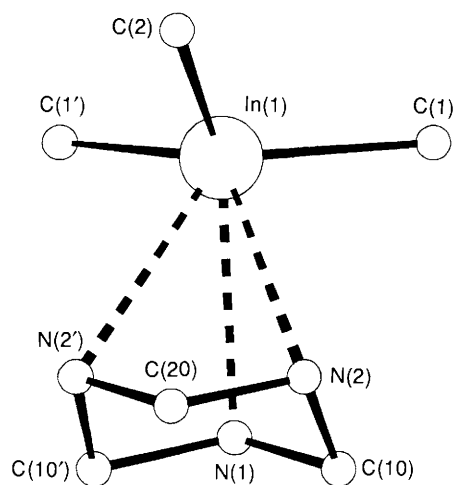


Fig. 1 The structure of $\text{Me}_3\text{In}(\text{Pr}^i\text{NCH}_2)_3$

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