Methylindium Dialkylamido Compounds: Mono- and Bis-Dialkylamides involving Four- and Five-co-ordinated Indium(III). *X*-Ray Crystal Structures of $\{Me_2In[N(CH_2)_2N(Me)CH_2CH_2]\}_2$, $MeIn[MeNC(CH)_4N]_2$, and $MeIn\{[MeN(CH_2)_2NMe]InMe_2\}_2$†

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The synthesis of $(Me_2InL)_2$ [L = $N(CH_2)_2N(Me)CH_2CH_2$ (**1**), $N(C_6H_{11})_2$ (**2**), and $NCH(Me)(CH_2)_3CHMe$ (**3**)] is reported. The *X*-ray crystal structure of (**1**) shows an amido-bridged dimer; all the compounds appear as dimers in the mass spectra. Variable-temperature ^1H n.m.r. of (**3**) shows that it exists as two conformational isomers which do not interconvert at room temperature. The synthesis of $MeIn[MeNC(CH)_4N]_2$ (**4**) and $MeIn\{[MeN(CH_2)_2NMe]InMe_2\}_2$ (**5**) is also reported and their *X*-ray crystal structures show square-pyramidal, bis(dialkylamido)metal centres; (**5**) also contains two peripheral, distorted tetrahedral indium atoms.

The chemistry of organo-indium compounds has recently received renewed attention because of their use as precursors for the metal-organic chemical vapour deposition[1] of single-crystal indium pnictides, which materials are of particular interest in the optoelectronics industry. The currently used indium precursors are the trialkyls or their adducts with tertiary amines and phosphines,[2] but we have endeavoured to find new, volatile dialkylamide compounds which could offer improvements over existing precursors.

Most of the previous indium dialkylamide compounds were amido-bridged dimers of the type $(R^1{}_2InNR^2{}_2)_2$ (*e.g.* R^1 = Me, R^2 = Me,[3] Et,[4] or Pr^i;[4] $NR^2{}_2$ = piperidide).[5] In these the indium atoms complete their octet by dimerizing and have distorted tetrahedral symmetry. Reported bis-dialkylamides largely comprise porphyrin[6,7] and phthalocyanine[8] systems which consequently show square-pyramidal metal centres.

Here we give examples of mono- and bis-dialkylamide compounds, one of which, (**5**), can be categorized as both; some of this work has been reported in a preliminary communication.[9]

Results and Discussion

Mono-dialkylamide Compounds.—Treatment of $InMe_2Cl$ with the *N*-lithiated derivatives of *N*-methylpiperazine, dicyclohexylamine, and 2,6-dimethylpiperidine in 1:1 molar ratio produced $\{Me_2In[N(CH_2)_2N(Me)CH_2CH_2]\}_2$ (**1**), $\{Me_2In[N(C_6H_{11})_2]\}_2$ (**2**), and $\{Me_2In[NCH(Me)(CH_2)_3CHMe]\}_2$ (**3**) respectively. Alternatively, (**1**) was also produced by facile methane elimination from a reaction between $Me_3In{\cdot}OEt_2$ and *N*-methylpiperazine. These compounds are white, crystalline solids which can be sublimed repeatedly *in vacuo*, although (**3**) decomposes just above the sublimation temperature used here (see below). They also react with air comparatively slowly; half-lives of one to several hours are typical when in the solid state. Analytical and physical data are given in Table 1, i.r. spectroscopic data in Table 2.

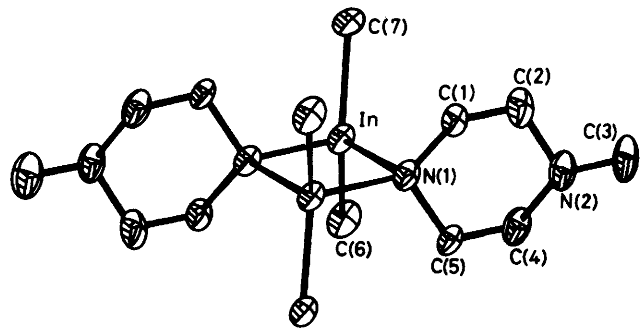


Figure 1. Molecular structure of $\{Me_2In[N(CH_2)_2N(Me)CH_2CH_2]_2\}$ (**1**) with the atomic numbering scheme

The evidence for the dimeric nature of the compounds comes from the mass spectra, all containing peaks in moderate abundance due to both dimer and monomer and/or the predicted fragmentation products therefrom, and the *X*-ray crystal structure of (**1**) (Figure 1 and Table 3). The centrosymmetric structure is analogous to other amido-bridged dimers,[3,4] consisting of a planar In_2N_2 unit with distorted tetrahedral metal environments. In theory, (**1**) could be monomeric if the amine function satisfied the indium octet by chelating; this would require the piperazine ring to adopt the less favoured boat conformation and, furthermore, the cyclic system thus formed may have to develop steric angle strain to attain effective overlap between the metal and amine lone pair. Instead these lone pairs project into space with no significant proximity to atoms on neighbouring molecules.

The ^1H n.m.r. spectra of (**1**) and (**2**), and most compounds of this type, show a singlet due to the Me–In resonance at *ca.* δ 0 p.p.m. That of (**3**), however, shows three signals in this region, a large central peak and two smaller peripheral peaks of equal intensity [Figure 2(*b*)]; furthermore, the doublet due to the piperidine methyl groups at δ 1.17 p.p.m. was observed on a high-field spectrometer (400 MHz) to be a large doublet at δ 1.17 with a smaller one at δ 1.18 p.p.m. [Figure 2(*a*)]. This is due to the existence of two conformational isomers (Figure 3). Isomer (**A**) has a centre of symmetry causing all the indium methyl groups to be equivalent and giving rise to the large

† Bis(μ-4-methylpiperazino-*N*)-tetramethyldi-indium(III), methylbis-[methyl(2-pyridyl)amido-*N*,*N'*]indium(III), and bis[μ_3-ethylene-bis(methylamido)-*N*($In^{1,2}$),*N'*($In^{2,3}$)]-1,1,2,3,3-pentamethyltri-indium(III) respectively.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: mmHg ≈ 133 Pa.

Table 1. Selected properties and analytical data for the compounds

Compound	M.p. (°C)		Accurate mass[a]	Analysis[a] (%) C	H	N
(1) $\{Me_2In[N(CH_2)_2N(Me)CH_2CH_2]\}_2$	186—189	Dimer	488.084 33 (488.086 07)	34.4 (34.5)	7.0 (7.0)	11.4 (11.5)
(2) $\{Me_2In[N(C_6H_{11})_2]\}_2$	170—173[b]	Monomer	325.126 91 (325.126 04)	51.1 (51.7)	8.6 (8.7)	4.4 (4.3)
(3) $\{Me_2In[NCH(Me)(CH_2)_3CHMe]\}_2$	124.5—125[c]	Monomer − H	256.054 87 (256.055 85)	41.8 (42.0)	7.7 (7.8)	5.4 (5.5)
(4) $MeIn[MeNC(CH)_4N]_2$	140 (decomp.)	Monomer	344.048 72 (344.049 18)	43.9 (45.4)	5.2 (5.0)	15.6 (16.3)
(5) $MeIn\{[MeN(CH_2)_2NMe]InMe_2\}_2$	195—200[d]	Monomer	591.997 76 (591.997 75)	25.4 (26.4)	5.8 (6.0)	9.0 (9.5)

[a] Required values are in parentheses. [b] Darkens to black at 150—160 °C. [c] Decomposes to a grey liquid at 125.5 °C. [d] Darkening at *ca.* 120 °C.

Table 2. Infrared spectroscopic data: ν(In–C)/cm^{-1}

Compound	Rocking mode	$\nu_{asym.}$	$\nu_{sym.}$
$(Me_2InNMe_2)_2$[a]	699	509	482
(1)	698	509	477
(2)	700	488[b]	471
(3)	707	502	486
(4)	703	—	510
(5)	696	502	481

[a] Data from ref. 3. [b] Assignment tentative.

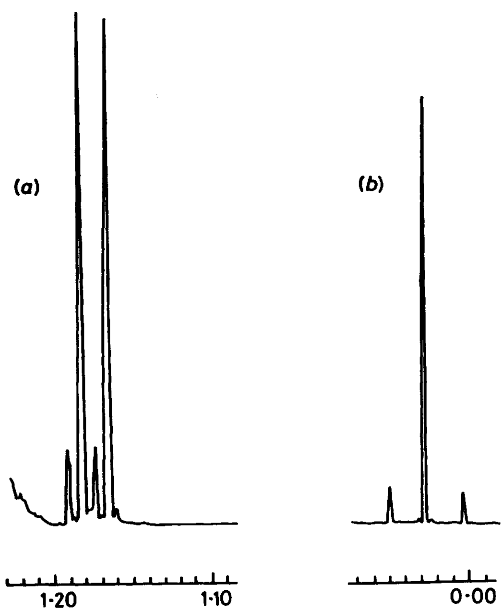


Figure 2. Selected peaks in the ^{1}H n.m.r. of $\{Me_2In[NCH(Me)(CH_2)_3CHMe]\}_2$ (3): (*a*) piperidide methyl and (*b*) indium methyl groups

Table 3. Selected bond lengths (Å) and angles (°) for compound (1)*

N(1)–In	2.230(5)	C(6)–In	2.161(6)
C(7)–In	2.163(6)	In–N(1a)	2.235(5)
C(1)–N(1)	1.476(6)	C(5)–N(1)	1.472(6)
C(2)–C(1)	1.505(8)	N(2)–C(2)	1.454(7)
C(3)–N(2)	1.456(7)	C(4)–N(2)	1.462(7)
C(5)–C(4)	1.522(8)		
C(6)–In–N(1)	109.6(2)	C(7)–In–N(1)	109.7(2)
C(7)–In–C(6)	128.9(3)	In–N(1)–In(a)	95.3(3)
C(1)–N(1)–In	115.2(3)	C(5)–N(1)–In	115.2(3)
C(5)–N(1)–C(1)	107.8(4)	N(1)–In–N(1a)	84.7(3)
C(2)–C(1)–N(1)	112.6(4)	N(2)–C(2)–C(1)	111.0(4)
C(3)–N(2)–C(2)	111.2(5)	C(4)–N(2)–C(2)	109.7(4)
C(4)–N(2)–C(3)	110.2(5)	C(5)–C(4)–N(2)	110.7(5)
C(4)–C(5)–N(1)	112.5(4)		

* Atoms designated (a) are related to those at *x*, *y*, *z* by the symmetry operation 1.0 − *x*, 1.0 − *y*, 1.0 − *z*.

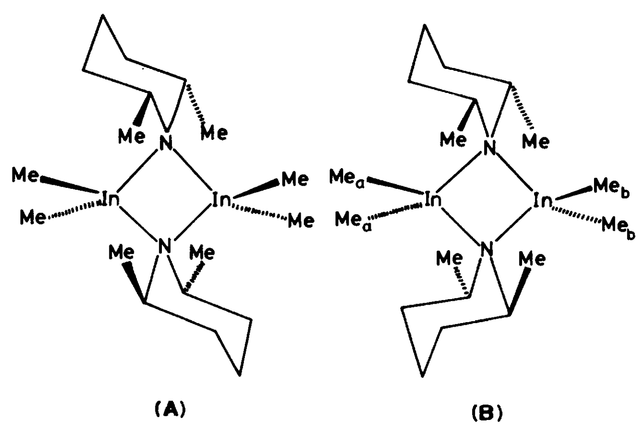
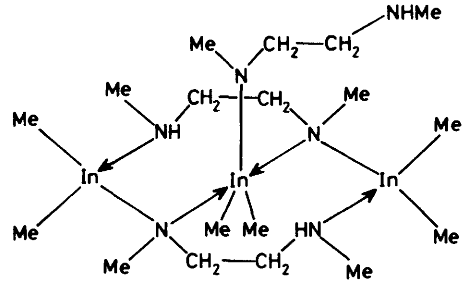


Figure 3. Conformational isomers of $\{Me_2In[NCH(Me)(CH_2)_3CHMe]\}_2$ (3)

singlet at δ 0.03 p.p.m. Isomer (**B**), however, has a plane of symmetry coplanar with the In_2N_2 unit, but no C_2 axis perpendicular to this plane; the indium methyls are of two types (a and b in Figure 3) and consequently give rise to the two equal signals at δ 0.01 and 0.05 p.p.m. Similar reasoning explains the signals around δ 1.18 p.p.m.

The ratio of the isomers (**A**):(**B**) at room temperature was 5.5:1, and this remained constant after one month in solution. The solution was then successively treated as follows and the spectra recorded: (*i*) after 180 min at 39 °C, ratio 3.5:1; (*ii*) after 30 min at 57 °C, ratio 1.3:1; (*iii*) after 30 min at 71 °C, ratio 1.0:1. At the last temperature the compound had partially decomposed to a grey solid, so the sample was cooled to room temperature; after 3 months at this temperature the ratio remained at 1:1. This is a clear indication that the initial ratio of 5.5:1 was a result of kinetic control, the thermodynamic equilibrium position giving roughly equal populations. Interconversion of these isomers requires breaking one amide bridge, inverting about the nitrogen atom and reforming the bridge; this does not occur to any measurable extent at room temperature.



(5a)

No attempt has been made to determine the activation energy for this interconversion, nor any attempt to isolate the isomers.

Bis-dialkylamide Compounds.—Treatment of $InMe_3$ with 2-(methylamino)pyridine in 1:2 molar ratio gave $MeIn[MeN\overline{C(CH)_4N}]_2$ (4), presumably with facile elimination of 2 equivalents of methane (gas evolution was noted). Treatment of $InMe_2Cl$ with mono-*N*-lithiated *N,N'*-dimethylethylenediamine gave $MeIn\{[MeN(CH_2)_2NMe]InMe_2\}_2$ (5). The initial product was probably $Me_2In[MeN(CH_2)_2NHMe]$ which then trimerized, perhaps to give (**5a**); subsequent loss of methane and metathesis between a peripheral N–H and a central covalent In–N bond would give (**5**). Interestingly, treatment of $InMe_3$ with $NH(Me)(CH_2)_2NHMe$ in 1:1 molar ratio could, in theory, by methane elimination give rise to (**5a**) and subsequently (**5**); this does not occur up to 90 °C (at 10^{-2} mmHg), when $Me_3In[NH(Me)(CH_2)_2NHMe]InMe_3$ sublimes out of the reaction mixture.[10]

The *X*-ray crystal structures of (**4**) and (**5**) (Figures 4 and 5, Tables 4 and 5 respectively) both contain square-pyramidal indium centres; to our knowledge, they are the first indium organometallics to do so besides the alkylindium porphyrins,[7] in which the metal co-ordination sphere is constrained by the ligand conformation. In (**5**) there is a central, square-pyramidal indium, the base formed by two chelating diamide ligands, with a methyl group apical. Each diamide also bridges two Me_2In units with distorted tetrahedral symmetry; thus (**5**) is also a mono-dialkylamide. The central metal is 0.93 Å above the square plane of the four nitrogens, as compared with 0.78 Å for methyl(5,10,15,20-tetraphenylporphyrinato)indium(III);[7] in (**4**), since the nitrogens are not perfectly planar, no exact, corresponding value can be given.

The In–N amide bond length in (**4**) is the shortest we have found, being 2.14 Å {*cf.* 2.23 Å for (**1**) (Table 3); 2.23 and 2.25 Å for $[Me_2In(NMe_2)]_2$[3]}, perhaps because it is non-bridging. The In–C bond (2.14 Å) is also very short compared with its previously found limits of 2.16—2.21 Å. This may be partly due to the geometry: in the porphyrin system the bond length is 2.13 Å;[7] however, in (**5**) the central In–C distance is 2.20 Å.

The ^1H n.m.r. spectrum of (**5**) shows three signals due to the indium methyls at δ −0.10, −0.03, and −0.01 p.p.m. in the ratio 1:2:2; the former is the apical methyl and the latter two are those on the Me_2In units proximal and distal to the apical methyl. The spectrum also shows a large singlet due to the N–Me groups superimposed on an AA'BB' multiplet due to the methylene protons.

The mass spectra of (**4**) and (**5**) show strong molecular ions with predicted fragmentation peaks.

Assignments of ν(In–C) i.r. vibrations for (**1**)—(**5**) are presented in Table 2. The spectrum of (**4**) shows ν(In–C) at 510 cm^{-1}, as compared with 490—500 cm^{-1} for methylindium porphyrins.[7] The corresponding vibration for (**5**) may be coincident with $\nu_{asym.}$ for the Me_2In unit, *i.e.* at 502 cm^{-1}.

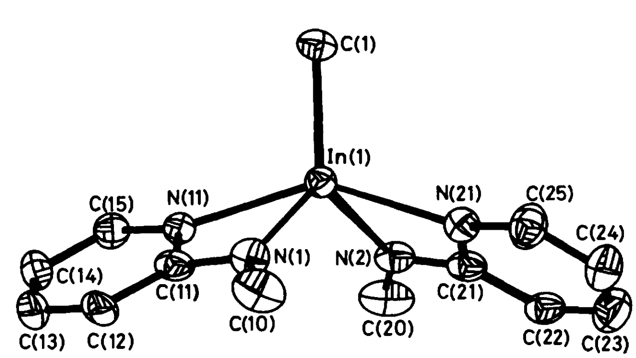


Figure 4. Molecular structure of $MeIn[MeN\overline{C(CH)_4N}]_2$ (4) with the atomic numbering scheme

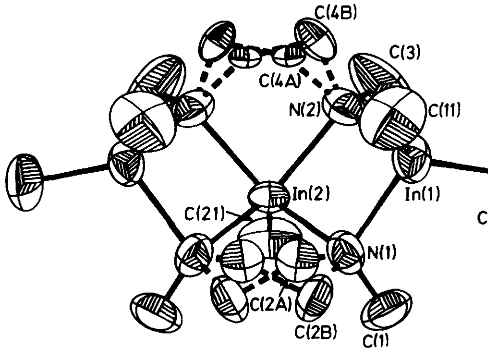


Figure 5. Molecular structure of $MeIn\{[MeN(CH_2)_2NMe]InMe_2\}_2$ (5) with the atomic numbering scheme

Experimental

All operations were performed under an atmosphere of purified nitrogen using Schlenk-style apparatus and a glove-box. Solvents were distilled from sodium benzophenone under nitrogen. Anhydrous $InCl_3$, all amines, and solutions of LiMe (in Et_2O) and $LiBu^n$ (in hexane), were obtained from commercial sources.

Hydrogen-1 n.m.r. spectra were obtained using Bruker WP80 FT and WH400 FT spectrometers. I.r. spectra were recorded as Nujol mulls between CsI plates using a Perkin-Elmer 577 spectrophotometer, and mass spectra using an AEI MS902 spectrometer (only principal peaks are reported; in the assignments, In refers to ^{115}In). Microanalyses were by the Microanalytical Laboratory of University College, London. The presence of indium was detected qualitatively by the performance of a simple flame test (purple).

Chlorodimethylindium was prepared by the literature method, treating $InCl_3$ with LiMe in a 1:2 molar ratio.[11] $InMe_3$ was prepared by thermal decomposition *in vacuo* of $(Me_3In)_2(Ph_2PCH_2CH_2PPh_2)$.[12]

Bis(μ-4-*methylpiperazino*-N)-*tetramethyldi-indium*(III), (**1**).—(*a*) n-Butyl-lithium (6.2 cm^3 of a 1.82 mol dm^{-3} solution, 12 mmol) was added to *N*-methylpiperazine (1.5 cm^3, 13 mmol) in diethyl ether (30 cm^3) at room temperature. The ether and excess amine were removed *in vacuo*, the residue redissolved in fresh diethyl ether (80 cm^3), and the solution was added to a stirred suspension of $InMe_2Cl$ (2.0 g, 11 mmol) in diethyl ether (60 cm^3). The white precipitate (LiCl) was filtered off and the clear, colourless filtrate was concentrated to 20 cm^3 *in vacuo* and held at −25 °C for 24 h, whence white *crystals* of (**1**) were obtained. These were sublimed at 90 °C (10^{-1} mmHg). Yield 1.3

Table 4. Selected bond lengths (Å) and angles (°) for compound (**4**)

N(11)–In(1)	2.351(5)	N(21)–In(1)	2.334(5)	C(12)–C(11)	1.421(7)	N(1)–C(11)	1.337(6)
N(2)–In(1)	2.138(5)	N(1)–In(1)	2.140(5)	C(22)–C(21)	1.405(7)	C(10)–N(1)	1.446(7)
C(1)–In(1)	2.137(7)	C(11)–N(11)	1.363(6)	C(14)–C(13)	1.379(9)	C(12)–C(13)	1.357(9)
C(15)–N(11)	1.334(6)	C(21)–N(21)	1.371(6)	C(24)–C(25)	1.363(8)	C(23)–C(22)	1.356(9)
C(25)–N(21)	1.342(6)	C(21)–N(2)	1.337(6)	C(14)–C(15)	1.376(8)	C(23)–C(24)	1.395(9)
C(20)–N(2)	1.447(7)						

N(21)–In(1)–N(11)	144.8(1)	N(2)–In(1)–N(11)	100.5(2)	C(20)–N(2)–C(21)	120.4(5)	N(1)–C(11)–N(11)	111.6(4)
N(2)–In(1)–N(21)	59.6(2)	N(1)–In(1)–N(11)	59.4(2)	C(12)–C(11)–N(11)	119.5(5)	C(12)–C(11)–N(1)	128.9(5)
N(1)–In(1)–N(21)	99.5(2)	N(1)–In(1)–N(2)	113.0(2)	C(11)–N(1)–In(1)	99.5(3)	C(10)–N(1)–In(1)	139.2(4)
C(1)–In(1)–N(11)	106.5(3)	C(1)–In(1)–N(21)	108.6(3)	C(10)–N(1)–C(11)	121.2(5)	N(2)–C(21)–N(21)	110.7(5)
C(1)–In(1)–N(2)	123.4(3)	C(1)–In(1)–N(1)	123.6(3)	C(22)–C(21)–N(21)	119.4(5)	C(22)–C(21)–N(2)	129.8(5)
C(11)–N(11)–In(1)	89.4(3)	C(15)–N(11)–In(1)	150.6(3)	C(14)–C(13)–C(12)	121.5(5)	C(23)–C(22)–C(21)	120.0(6)
C(15)–N(11)–C(11)	119.9(5)	C(21)–N(21)–In(1)	90.0(3)	C(13)–C(12)–C(11)	118.6(6)	C(24)–C(25)–N(21)	123.8(6)
C(25)–N(21)–In(1)	151.1(3)	C(25)–N(21)–C(21)	118.9(5)	C(23)–C(24)–C(25)	117.6(6)	C(24)–C(23)–C(22)	120.3(6)
C(21)–N(2)–In(1)	99.7(3)	C(20)–N(2)–In(1)	139.8(3)	C(14)–C(15)–N(11)	122.7(6)	C(15)–C(14)–C(13)	117.8(6)

Table 5. Bond lengths (Å) and angles (°) for compound (**5**)

N(1)–In(1)	2.210(9)	N(2)–In(1)	2.193(10)	C(2A)–N(1)	1.580(24)	C(2B)–N(1)	1.452(30)
C(11)–In(1)	2.187(13)	C(12)–In(1)	2.182(13)	C(3)–N(2)	1.495(14)	C(4A)–N(2)	1.646(26)
N(1)–In(2)	2.283(9)	N(2)–In(2)	2.255(10)	C(4B)–N(2)	1.417(31)	C(2A)–C(2BB)	1.539(18)
C(21)–In(2)	2.198(15)	C(1)–N(1)	1.472(14)	C(4A)–C(4BB)	1.555(15)		

N(2)–In(1)–N(1)	84.7(4)	C(11)–In(1)–N(1)	111.8(6)	In(2)–N(2)–In(1)	97.4(4)	C(3)–N(2)–In(1)	112.9(9)
C(11)–In(1)–N(2)	110.6(5)	C(12)–In(1)–N(1)	108.2(5)	C(3)–N(2)–In(2)	112.9(8)	C(4A)–N(2)–In(1)	106.3(10)
C(12)–In(1)–N(2)	108.8(6)	C(12)–In(1)–C(11)	125.3(6)	C(4A)–N(2)–In(2)	98.3(9)	C(4A)–N(2)–C(3)	124.8(13)
N(2)–In(2)–N(1)	81.6(4)	C(21)–In(2)–N(1)	114.1(5)	C(4B)–N(2)–In(1)	125.2(17)	C(4B)–N(2)–In(2)	117.9(14)
C(21)–In(2)–N(2)	114.4(5)	In(2)–N(1)–In(1)	96.1(4)	C(4B)–N(2)–C(3)	91.4(15)	C(4B)–N(2)–C(4A)	33.5(11)
C(1)–N(1)–In(1)	112.3(8)	C(1)–N(1)–In(2)	114.5(8)	N(2)–In(2)–N(2)	79.2(6)	C(4B)–C(4A)–N(2)	59.3(28)
C(2A)–N(1)–In(1)	105.7(11)	C(2A)–N(1)–In(2)	100.3(9)	C(4A)–C(4B)–N(2)	87.2(30)	C(2B)–C(2A)–N(1)	65.7(30)
C(2A)–N(1)–C(1)	123.9(12)	C(2B)–N(1)–In(1)	129.3(15)	C(2A)–C(2B)–N(1)	82.5(31)	N(2)–C(2A)–C(2BB)	110.8(13)
C(2B)–N(1)–In(2)	113.3(13)	C(2B)–N(1)–C(1)	92.5(13)	N(1)–C(2B)–C(2AB)	104.4(11)	N(2)–C(4A)–C(4BB)	113.9(8)
C(2B)–N(1)–C(2A)	31.8(11)	N(1)–In(2)–N(1)	78.6(5)	N(2)–C(4B)–C(4AB)	100.7(10)		

g, 48% based on $InMe_2Cl$. I.r. (cm^{-1}): several bands at *ca.* 2 800 (m to s), 1 446s, 1 364s, 1 307w, 1 289s, 1 280s, 1 203w, 1 159m, 1 150s, 1 137s, 1 119s, 1 087m, 1 048m, 1 003s, 969w br, 909m, 876s br, 860m (sh), 787m, 775m, 699vs vbr, 668s, 509s, 493m, 477s, 456m, 394m, 324w br, 292w. N.m.r.: δ_H (80 MHz, C_6D_6) −0.02 (12 H, s, MeIn), 2.08 (6 H, s, NMe), 2.15 (8 H, m, $InNCH_2$), 3.01 p.p.m. (8 H, m, $MeNCH_2$): Mass spectrum: m/z 488 [18%, dimer (2*M*)], 473 (13, 2*M* − Me), 390 [11, 2*M* − $MeN_2C_4H_8$(amide) + H], 389 (87, 2*M* − amide), 375 (16, 2*M* − amide − CH_2), 244 [9, monomer (*M*)], 213 (17, *M* − 2Me − H), 145 (33, Me_2In), 115 (30, In).

(*b*) Methyl-lithium (53 cm^3 of a 1.67 mol dm^{-3} solution, 89 mmol) was added dropwise to a stirred suspension of $InCl_3$ (6.4 g, 29 mmol) in diethyl ether (50 cm^3). The contents were allowed to warm to room temperature and the white precipitate filtered off. To the clear, colourless filtrate was added *N*-methylpiperazine (3.0 g, 30 mmol), after which solvent was removed *in vacuo* to leave a white residue. This was sublimed at 90 °C (10^{-1} mmHg) to give white *crystals* of (**1**). Yield 4.3 g, 61% based on $InCl_3$.

Bis(μ-*dicyclohexylamido*)-*tetramethyldi-indium*(III), (**2**).—This was prepared in a similar manner to (**1**) using $LiBu^n$ (6.3 cm^3 of a 1.67 mol dm^{-3} solution, 11 mmol), $NH(C_6H_{11})_2$ (2.2 cm^3, 11 mmol), and $InMe_2Cl$ (1.9 g, 11 mmol). The product was recrystallized from diethyl ether as white, fluffy *crystals* of (**2**). Yield 2.0 g, 56% based on $InMe_2Cl$. I.r. (cm^{-1}): 1 451vs, 1 369m, 1 350m, 1 334w, 1 302w, 1 277w, 1 253w, 1 244w, 1 169m, 1 156m, 1 140w, 1 106m, 1 091m, 1 081m, 1 060s br, 1 035s (sh), 1 029s br, 976m, 943s (sh), 936s, 924m br, 900s, 883w, 843m, 805w, 789w, 780m, 701vs vbr, 656m, 639m, 582s, 572m, 543m, 488s, 471s, 441w, 431m br, 340w br, 232w. N.m.r.: δ_H (80 MHz, C_6D_6) 0.22 (12 H, s, MeIn), 0.9—2.1 (40 H, br m, CH_2), 3.15 p.p.m. (4 H, m, CH). Mass spectrum: m/z 650 [1%, dimer 2*M*], 635 (2, 2*M* − Me), 470 [4, 2*M* − $N(C_6H_{11})_2$-(amide)], 325 [2, monomer (*M*)], 310 (9, *M* − Me), 181 [19, $NH(C_6H_{11})_2$], 145 (13, Me_2In), 138 (100, amide − C_3H_8), 115 (4, In), 98 (13, amine − C_6H_{11}).

Bis(μ-*2,6-dimethylpiperidino*-N)-*tetramethyldi-indium*(III), (**3**).—This was prepared in a similar manner to (**1**) using $LiBu^n$ (14.5 cm^3 of a 1.91 mol dm^{-3} solution, 28 mmol), 2,6-dimethylpiperidine (4.3 cm^3, 30 mmol) and $InMe_2Cl$ (4.9 g, 27 mmol). The product was carefully sublimed at 78 °C (10^{-2} mmHg) as white *crystals* of (**3**). Yield: 4.1 g, 59% based on $InMe_2Cl$. (Note: at temperatures above 80 °C gradual decomposition occurs.) I.r. (cm^{-1}): 1 444s, 1 358m, 1 351m, 1 332w, 1 316m, 1 304m, 1 274w, 1 212s, 1 184w, 1 163s, 1 144s, 1 130s, 1 115s, 1 066s, 1 022m, 997m, 973m, 953s, 930m, 915m, 844s, 807w, 743s, 708vs br, 691s, 664m br, 652m, 621s, 559w, 502s, 491s, 487s (sh), 433w, 386w, 353w, 318w br. N.m.r.: δ_H (80 MHz, $C_6D_5CD_3$) *ca.* 0.03 (12 H, 3 peaks, MeIn), 0.9—1.7 (12 H, br m, CH_2), 1.17 (12 H, d, *J* 7 Hz, CH*Me*), 3.20 p.p.m. (4 H, br m, CH). Mass spectrum: m/z 499 [14%, dimer (2*M*) − Me], 402 (20, 2*M* − Me_2In), 257 [5, monomer (*M*)], 256 (38, *M* − H), 242 (25, *M* − Me), 145 (21, Me_2In), 115 (32, In).

Methylbis[*methyl*(*2-pyridyl*)*amido*-N,N′]*indium*(III), (**4**).—Freshly sublimed $InMe_3$ (0.64 g, 4 mmol) was cooled to − 196 °C and 2-(methylamino)pyridine (0.9 g, 8 mmol) was

Table 6. Crystal data, details of intensity measurements and structure refinement for compounds (**1**), (**4**), and (**5**)

Compound	(**1**)	(**4**)	(**5**)
Formula	$[C_7H_{17}InN_2]_2$	$C_{13}H_{17}InN_4$	$C_{13}H_{35}In_3N_4$
M	488.052	346.122	591.850
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_1/a$ [a]	$Pnam$ [b]
a/Å	8.256(3)	8.094(2)	15.039(2)
b/Å	9.363(3)	20.592(2)	8.497(1)
c/Å	7.503(4)	8.802(3)	17.006(2)
α/°	105.28(3)	90.0	90.0
β/°	115.68(4)	94.76(4)	90.0
γ/°	95.226(3)	90.0	90.0
U/Å^3	489.92	1 462.97	2 173.19
Z	2	4	4
D_c/g cm^{-3}	1.654	1.572	1.808
F(000)	123	696	1 152
μ/cm^{-1}	10.84	14.70	29.19
θ range (°)	1.5, 25.0	1.5, 25.0	2.0, 25.0
h, k, l range	−11—11, −10—10, 0—8	0—9, 0—24, −10—10	0—17, 0—20, 0—10
Total no. of reflections	1 905	2 856	2 200
No. of unique reflections	1 710	2 580	1 972
Significance test	$F_o > 3\sigma(F_o)$	$F_o > 3\sigma(F_o)$	$F_o > 3\sigma(F_o)$
No. of observed reflections	1 605	2 007	1 411
No. of refined parameters	132	222	112
Max. least-squares shift/e.s.d.	−0.063	−0.281	−0.055
Min., max. heights in final difference map (e Å^{-3})	−0.854, 0.745	−0.488, 0.462	−0.842, 0.623
Weighting scheme parameter g in $w = 1/[\sigma^2(F) + gF^2]$	0.000 15	0.000 10	0.000 02
Final R [c]	0.0300	0.0286	0.0430
Final R' [d]	0.0328	0.0278	0.0403

[a] Alternative setting of $P2_1/c$ (no. 14). Symmetry operations: x, y, z; $-x, -y, -z$; $\frac{1}{2}+x, \frac{1}{2}-y, z$; $\frac{1}{2}-x, \frac{1}{2}+y, -z$. [b] Alternative setting of $Pnma$ (no. 62). Symmetry operations: x, y, z; $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$; $-x, -y, \frac{1}{2}+z$; $\frac{1}{2}-x, \frac{1}{2}+y, -z$; $-x, -y, -z$; $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; $x, y, \frac{1}{2}-z$; $\frac{1}{2}+x, \frac{1}{2}-y, z$. [c] $R = \Sigma|\Delta F|/\Sigma|F_o|$. [d] $R' = [\Sigma w|\Delta F|^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

Table 7. Fractional atomic co-ordinates (× 10^4) for compound (**1**)

Atom	x	y	z
In	3 501	3 354	3 449
N(1)	6 426(4)	4 415(4)	4 460(5)
C(1)	6 788(5)	4 611(5)	2 767(6)
C(2)	6 798(6)	3 132(5)	1 363(6)
N(2)	8 185(5)	2 427(5)	2 562(6)
C(3)	8 190(7)	991(6)	1 212(8)
C(4)	7 834(6)	2 178(5)	4 219(7)
C(5)	7 811(5)	3 669(5)	5 632(6)
C(6)	3 440(6)	1 671(5)	4 927(7)
C(7)	1 753(6)	3 230(5)	249(6)

condensed on to it *in vacuo*. The mixture was gradually warmed to room temperature and at *ca.* 0 °C the $InMe_3$ dissolved in the amine with rapid evolution of gas bubbles. The resulting pale yellow liquid was heated to 50 °C for 30 min to complete reaction, dissolved in pentane (50 cm^3), and held at −25 °C whence off-white *crystals* of (**4**) were obtained. Yield 1.0 g, 72% based on $InMe_3$. I.r. (cm^{-1}): *ca.* 1 600vs vbr, 1 543m, strong

Table 8. Fractional atomic co-ordinates (× 10^4) for compound (**4**)

Atom	x	y	z
In(1)	−504(0.5)	3 303(0.5)	137(0.5)
N(11)	1 105(4)	3 234(2)	2 480(4)
N(21)	−2 063(4)	3 994(2)	−1 523(4)
N(2)	638(4)	4 115(2)	−867(4)
C(11)	−240(5)	3 420(2)	3 207(4)
N(1)	−1 550(4)	3 541(2)	2 220(4)
C(21)	−676(5)	4 359(2)	−1 697(4)
C(13)	1 370(8)	3 327(3)	5 595(5)
C(22)	−787(7)	4 899(2)	−2 677(6)
C(12)	−108(7)	3 467(2)	4 822(5)
C(25)	−3 504(6)	4 170(2)	−2 273(5)
C(20)	2 234(6)	4 433(3)	−841(7)
C(24)	−3 675(7)	4 692(3)	−3 225(6)
C(23)	−2 267(8)	5 065(3)	−3 407(6)
C(1)	−559(7)	2 349(2)	−824(6)
C(15)	2 525(6)	3 089(2)	3 287(5)
C(14)	2 718(8)	3 132(3)	4 851(6)
C(10)	−3 110(7)	3 755(4)	2 737(8)

Table 9. Fractional atomic co-ordinates (× 10^4) for compound (**5**)

Atom	x	y	z
In(1)	1 427(1)	940(1)	897(0.5)
In(2)	1 965(1)	−1 123(1)	2 500
N(1)	2 610(5)	616(9)	1 650(4)
N(2)	821(5)	−852(10)	1 655(5)
C(21)	2 580(10)	−3 469(16)	2 500
C(11)	802(10)	3 232(14)	1 087(8)
C(1)	3 373(8)	−19(19)	1 211(8)
C(12)	1 705(10)	−107(19)	−249(6)
C(3)	607(12)	−2 339(15)	1 226(9)
C(4A)	131(13)	90(30)	2 240(12)
C(4B)	−50(19)	−777(40)	1 971(17)
C(2A)	2 657(15)	2 129(24)	2 188(13)
C(2B)	3 154(18)	1 791(38)	2 040(16)

peaks 1 450—1 510, 1 414s br, 1 368s (sh), 1 336m, 1 300s, 1 290s, 1 276m, 1 165s, 1 154s, 1 127w br, 1 082m, 1 042w, 1 029w, 993w (sh), 982m, 952w, 832m (sh), 824s, 819s, 771vs br, 732vs, 702vs vbr, 644s, 599m, 574m br, 520s (sh), 510s, 478m (sh), 449s br, 419s, 308m br, 283w (sh), 243w. N.m.r.: δ_H (80 MHz, C_6D_6) 0.28 (3 H, s, MeIn), 2.71 (6 H, s, NMe), 6.00—7.68 p.p.m. (8 H, 3 distinct multiplets, aromatic protons). Mass spectrum: m/z 344 (12%, M), 329 (30, M − Me), 237 [30, M − $MeNC_5H_4N$(amide)], 222 (47, M − amide − Me), 221 [25, M − $MeNHC_5H_4N$(amine) − Me], 145 (3, Me_2In), 115 (39, In), 107 (100, amide), 106 (58, amide − H).

Bis[μ_3-*ethylenebis*(*methylamido*)-N(*In*^{1,2}),N′(*In*^{2,3})]-1,1,2,3,3-*pentamethyltri-indium*(III), (**5**).—n-Butyl-lithium (15 cm^3 of a 1.91 mol dm^{-3} solution, 29 mmol) was added to *N,N′*-dimethylethylenediamine (2.9 cm^3, 30 mmol) in diethyl ether (30 cm^3) at 0 °C; upon warming to room temperature a copious, white precipitate appeared. Diethyl ether and excess amine were removed *in vacuo* and the viscous, yellow liquid residue was redissolved in diethyl ether (60 cm^3) and added to $InMe_2Cl$ (5.1 g, 28 mmol) suspended in diethyl ether (50 cm^3). The contents were heated to reflux for 60 min, cooled to room temperature and the precipitate filtered off. The filtrate was concentrated to 10 cm^3 *in vacuo* and held at −25 °C whence white *crystals* of (**5**) were obtained. These were sublimed at 90 °C (10^{-2} mmHg). Yield 3.5 g, 63% based on $InMe_2Cl$. I.r. (cm^{-1}): 2 790s, 1 412w, 1 358m, 1 339m, 1 299w br, 1 276m, 1 237m, 1 189w, 1 159m (sh), 1 154s, 1 130w, 1 121m, 1 110m, 1 084m, 1 032m, 997s, 965s, 851vs, 696vs vbr, 611m, 604m, 502vs, 481s, 444s, 420m br (sh), 358s br, 314m br. N.m.r.: δ_H (80 MHz, C_6D_6) −0.10, (3 H, s, apical MeIn), −0.03 and −0.01 (12 H, 2 singlets due to MeIn proximal and distal to the apical MeIn), 2.50 (12 H, s, NMe), 2.75 p.p.m. (8 H, AA′BB′, CH_2); δ_C (20.1 MHz, C_6D_6) −10.7, −10.5, −10.3 (MeIn), 43.0 (NMe), 54.9 p.p.m. (CH_2). Mass spectrum: *m/z* 592 (30%, *M*), 577 (28, *M* − Me), 549 (54, *M* − CH_2NMe), 534 (25, *M* − CH_2NMe − Me), 492 [13, *M* − $(MeNCH_2)_2$(amide) − CH_2], 491 (100, *M* − amide − Me), 489 (16, *M* − amide − Me − 2H), 461 (11, *M* − MeIn − H), 431 (10, *M* − Me_2In − CH_4), 331 (43, *M* − 2MeIn − H), 301 (16, *M* − 2Me_2In − H), 217 (11, MeIn + amide + H), 215 (75, MeIn + amide − H), 201 (15, In + amide), 200 (13, In + amide − H), 199 (28, In + amide − 2H), 158 (23, InCH_2NMe), 145 (26, Me_2In), 115 (54, In), 88 (25, amide + 2H).

X-*Ray Crystallography*.—Crystals of (**1**), (**4**), and (**5**) used for the *X*-ray work were sealed under argon in thin-walled glass capillaries. All crystallographic measurements were made at 293 K using a Nonius CAD4 diffractometer and graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å), following previously detailed procedures.[13] The structures were solved *via* the heavy-atom method and refined by full-matrix least squares. For compound (**1**), all non-hydrogen atoms were refined anisotropically; hydrogen atoms were included and refined isotropically with those in methyl groups constrained to idealized positions. For compound (**4**), non-hydrogen atoms were refined anisotropically; hydrogens were included at experimentally determined positions and freely refined isotropically. For compound (**5**), conformational disorder occurred in the bridging –CH_2CH_2– groups of the co-ordinating diamides. Each of these atoms were represented by a split site, with two half atoms included and refined isotropically. All other non-hydrogen atoms were refined anisotropically, but no hydrogens were included for this structure.

Details of the crystal data, data collection, and refinement are given in Table 6. Atomic co-ordinates are given in Tables 7—9. Computer programs and sources of scattering factor data were as previously described.[13]

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