Synthesis and Structural Studies of Dimethylindium(III) Complexes with Polydentate Nitrogen Donor Ligands, and of Monomethylindium(III) Complexes containing Alkoxide-bridged Binuclear Cations *

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Dimethylindium(III) complexes have been isolated from aqueous methanol on reaction of dimethylindium(III) nitrate with the neutral nitrogen donor ligands 1,10-phenanthroline, 2,2′-bipyridyl, and 4,4′disubstituted 2,2′-bipyridyls, bis(pyridin-2-yl)methane [$(py)_2CH_2$], bis(*N*-methylimidazol-2-yl)methanol, 2,2′:6′,2″-terpyridyl (terpy), 4,4′,4″-triethyl-2,2′:6′,2″-terpyridyl (Et_3terpy), and *N*-methyl-2-(pyridin-2-yl)imidazole. *X*-Ray crystallographic studies at 295 K of two of the complexes reveal the formulations [$InMe_2\{(py)_2CH_2$-*N,N*$\}(NO_3$-*O*$)(H_2O)$] (**5**) and [$InMe_2(Et_3$terpy-*N,N′,N″*)]NO_3 (**8**), with *trans* methyl groups in distorted octahedral [for (**5**)] and five-co-ordinate geometry [for (**8**)]. The complexes have In–C 2.119(7)—2.131 (8) Å and In–N bond distances 2.310(5)—2.439(4) Å, with In–O 2.632(4) Å (NO_3) and 2.679(5) Å (H_2O) in (**5**); the $InMe_2$ groups are bent away from the nitrogen donor ligands, forming InC_2 angles of 157.6(2) [(**5**)] and 132.8(3)° [(**8**)]. The $In^{III}Me_2$ complexes of terpy [(**7**)] and Et_3terpy [(**8**)] are photochromic, changing slowly from pale yellow to emerald green in bright light, and back to yellow in darkness. Reaction of [$InMe_2$]NO_3 with phenylbis(pyridin-2-yl)methanol [$(py)_2(Ph)COH$], tris(pyridin-2-yl)methanol, tris(*N*-methylimidazol-2-yl)methanol, bis(*N*-methylimidazol-2-yl)(pyridin-2-yl)methanol [$(py)(mim)_2COH$], and (*N*-methylimidazol-2-yl)bis(pyridin-2-yl)methanol, results in isolation of monomethylindium(III) complexes containing binuclear cations, with the structures of two of these established crystallographically as [$InMe(H_2O)\{\mu$-$(py)_2(Ph)CO$-*N,N′*,μ-*O*$\}_2InMe(NO_3)$]$NO_3\cdot0.75H_2O$ (**10**) and [$InMe(H_2O)\{\mu$-$(py)(mim)_2CO$-*N,N′*,μ-*O*$\}_2InMe(NO_3)$]$NO_3\cdot H_2O\cdot Me_2CO$ (**13**). Each ligand has a py group co-ordinated to one indium atom and a py [(**10**)] or mim [(**13**)] group co-ordinated to the other indium, with alkoxide bridges forming an In_2O_2 kernel with In–O distances 2.165(6)—2.266(6) Å and *trans* methyl groups for the 'equatorial' planes $In_2Me_2(py)_2(\mu$-$O)_2$ [(**10**)] and $In_2Me_2(mim)_2(\mu$-$O)_2$ [(**13**)]. Indium–carbon, 2.119(11)—2.160(13) Å, and In–N bond distances, 2.234(7)—2.409(9) Å, are similar to those for the $In^{III}Me_2$ complexes. Six-co-ordination for one indium is completed by a water molecule [2.304(9) in (**10**), 2.300(6) Å in (**13**))], and a nitrate group interacts unsymmetrically with the other indium [In-O 2.422(12) in (**10**), 2.387(7) Å in (**13**); In • • • O 2.692(15) in (**10**), 2.802(9) Å in (**13**)], with both aqua and nitrate groups *trans* to 'axial' py groups in both complexes. The geometry at the indium atoms in (**10**) and (**13**) is irregular, but, except for the orientation of the more weakly co-ordinating aqua and nitrate groups in each complex, the indium atoms have similar geometry, with analogous donor atoms of the other five groups subtending angles at indium within 6 [(**10**)] and 2° [(**13**)] of each other. The $In^{III}Me_2$ and $In^{III}Me$ complexes form conducting solutions with retention of nitrogen donor co-ordination; the binuclear complexes exhibit complex variable-temperature ^1H n.m.r. spectra in CD_3OD resulting from the presence of exchange between nitrogen donor sites and also between isomers for complexes of ligands containing both py and mim donor groups. Crystals of (**5**), (**8**), and (**13**) are monoclinic, space group $P2_1/c$, and (**10**) is triclinic, space group $P\bar{1}$; (**5**) has a = 9.002(3), b = 12.538(7), c = 13.996(7) Å, β = 91.26(3)°, Z = 4; (**8**) has a = 8.641(3), b = 15.872(6), c = 17.242(7) Å, β = 90.78(3)°, Z = 4; (**10**) has a = 19.147(5), b = 11.007(4), c = 9.486(8)°, α = 76.14(6), β = 88.79(6), γ = 87.87(3)°, Z = 2; (**13**) has a = 14.388(6), b = 17.613(10), c = 16.403(10) Å, β = 92.18(3)° Z = 4. Residuals were 0.033, 0.047, 0.064, and 0.052 for 2 155, 2 502, 4 486, and 3 676 independent reflections, respectively.

There are few reports of structural studies of organoindium(III) complexes containing neutral donor ligands,[1–4] and in one of these the donor group is part of an intramolecular organoindium(III) system,[1] chlorobis{2-[(dimethylamino)methyl]phenyl-*N,C*}indium(III). In these complexes, as in other structurally characterized organoindium(III) complexes with anionic polydentate ligands, the anion groups are strongly co-ordinated,[1–8] *e.g.* the chloro group in the above complex[1] and the oximate oxygen in bis[dimethyl(pyridine-2-carbaldehyde oximato-*N,N′,O*)indium(III)].[7] In contrast, for the diorganothallium(III) ion, several structural studies have been

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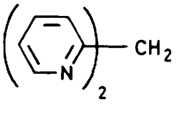
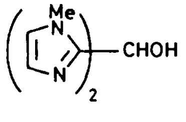
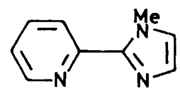
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.



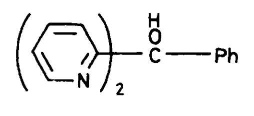
$(py)_2CH_2$



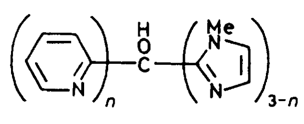
$(mim)_2CHOH$



pymim



$(py)_2(Ph)COH$



$n = 0$: $(mim)_3COH$
$n = 1$: $(py)(mim)_2COH$
$n = 2$: $(py)_2(mim)COH$
$n = 3$: $(py)_3COH$

reported for complexes of neutral donor ligands in which the anions are unco-ordinated or weakly co-ordinated,[9–13] *e.g.* the 2,2′:6′,2″-terpyridyl (terpy) complex $[TlMe_2(terpy\text{-}N,N',N'')(H_2O)]NO_3$ which has an ionic nitrate group [Tl$\cdots$$ONO_2$ 3.250(19) Å].[12]

We report here the synthesis of dimethylindium(III) complexes with neutral nitrogen donor ligands in aqueous methanol, where the anion, nitrate, is expected to be unco-ordinated or only weakly co-ordinated. Studies were initially confined to 1,10-phenanthroline (phen), bis(pyridine-2-yl)-methane $[(py)_2CH_2]$, terpy, and 4,4′,4″-triethyl-2,2′:6′,2″-terpyridyl (Et_3terpy), as structural studies have been reported for dimethylthallium(III) complexes of these ligands.[9,12] The closely related ligands bis(*N*-methylimidazol-2-yl)methanol $[(mim)_2CHOH]$, *N*-methyl-2-(pyridin-2-yl)imidazole (pymim), and 4,4′-substituted 2,2′-bipyridyls [dimethyl (Me_2bipy) and diethyl (Et_2bipy)] were subsequently included. Structural studies reveal

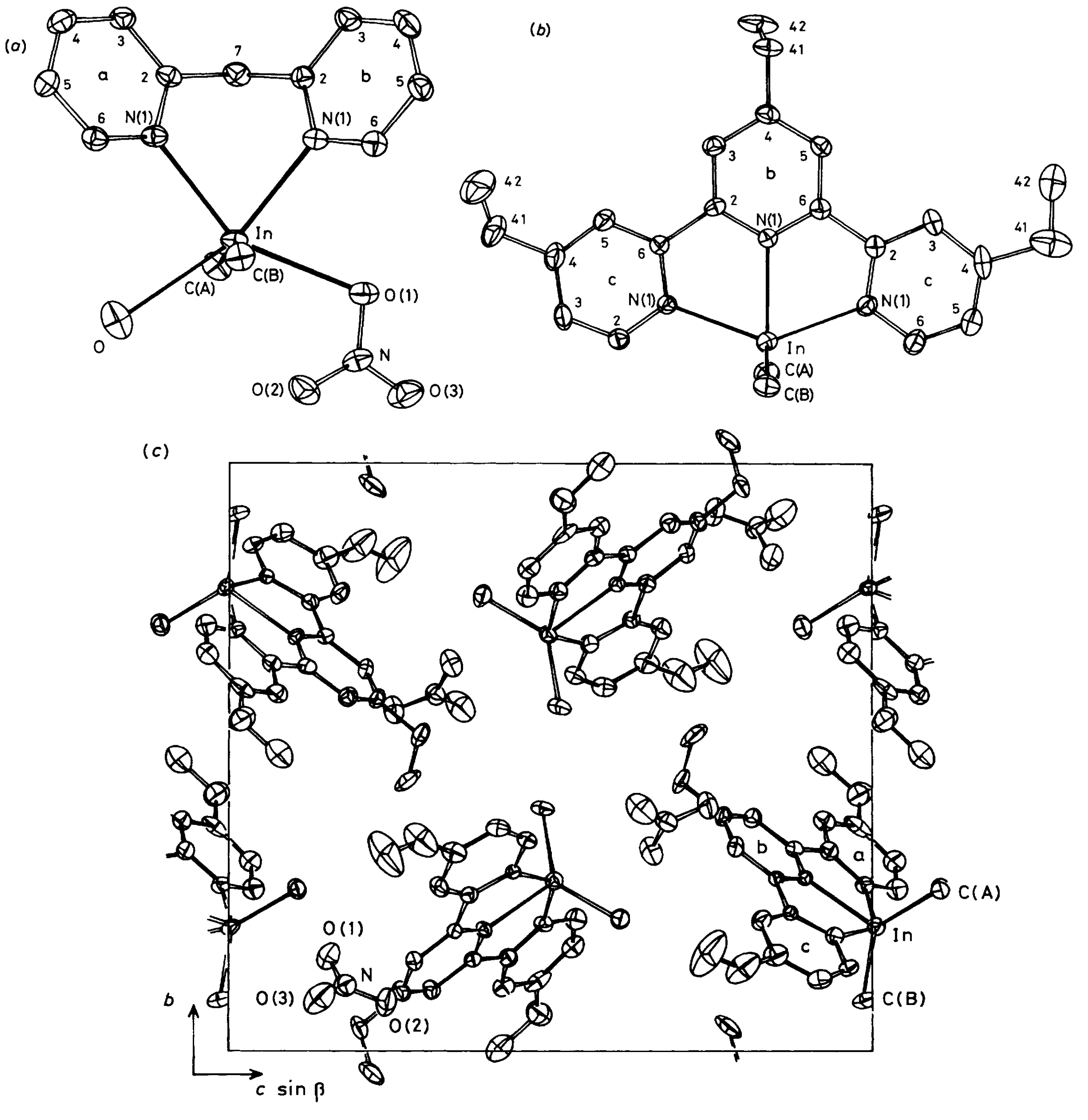


Figure 1. Structures of (*a*) $[InMe_2\{(py)_2CH_2\text{-}N,N'\}(NO_3\text{-}O)(H_2O)]$ (**5**), (*b*) $[InMe_2(Et_3terpy\text{-}N,N',N'')]^+$ in its nitrate salt (**8**), with projections normal to the 'equatorial planes' in each case, and (*c*) unit-cell contents of (**8**), projected down *a*; 20% thermal ellipsoids are shown for the non-hydrogen atoms together with atom numbering. Hydrogen atoms have been omitted to improve clarity

Table 1. Characterization data for the complexes

	Analysis[a] (%)			Λ_M[b]/Ω^{-1} cm^2 mol^{-1}	^{1}H N.m.r.[c]	
Complex stoicheiometry	C	H	N		δ(InMe)	Ligand
(**1**) $[InMe_2(phen)]NO_3$[d]	43.4 (43.4)	3.6 (3.6)	10.7 (10.9)	76	−0.01,**6**	9.27, **2**, *dd*, H(2,9); 8.84, **2**, *dd*, H(4,7); 8.21, **2**, *s*, H(5,6); 8.10, **2**, *dd*, H(3,8)[e]
(**2**) $[InMe_2(bipy)]NO_3$	40.1 (39.7)	4.0 (3.9)	11.7 (11.6)	74	−0.08,**6**	8.87, **2**, *ddd*, H(6); 8.54, **2**, *m*, H(3); 8.23, **2**, '*td*', H(4); 7.74, **2**, *m*, H(5)[f]
(**3**) $[InMe_2(Me_2bipy)]NO_3$[d]	43.6 (43.0)	4.7 (4.6)	11.0 (10.7)	88	−0.10,**6**	8.67, **2**, *m* (*br*), H(6); 8.42, **2**, *s* (*br*), H(3); 7.59, **2**, *d* (*br*), H(5); 2.60, **6**, *s*, CH$_3$[g]
(**4**) $[InMe_2(Et_2bipy)]NO_3$[d]	45.4 (45.8)	5.4 (5.3)	9.9 (10.0)	77	−0.10,**6**	8.71, **2**, *d*, H(6); 8.45, **2**, *s*, H(3); 7.61, **2**, *dd*, H(5); 4.47, **4**, *q*, CH$_2$; 2.94, **6**, *t*, CH$_3$[h]
(**5**) $[InMe_2\{(py)_2CH_2\}(NO_3)(H_2O)]$[i]	40.6 (39.5)	4.7 (4.6)	11.1 (10.6)	83	+0.04,**6**	8.53, **2**, *m*, H(6); 7.89, **2**, '*td*', H(4); 7.51, **2**, *d*, H(3); 7.40, **2**, *m*, H(5); 4.40, **2**, *s*, CH$_2$[j]
(**6**) $[InMe_2\{(mim)_2CHOH\}]NO_3$[k]	33.1 (33.1)	4.3 (4.5)	17.6 (17.5)	88	−0.12,**6**	7.29, **2**, *s*, and 7.16, **2**, *s*, H(4,5); 6.23, **1**, *s*, CH; 3.91, **6**, *s*, CH$_3$
(**7**) $[InMe_2(terpy)]NO_3 \cdot H_2O$[l,m]	44.5 (44.6)	4.2 (4.2)	12.2 (12.2)	93	−0.10,**6**	8.89, **2**, *d* (*br*), H(6,6″); 8.81, **2**, *d*, H(3′,5′); 8.72, **2**, *m*, H(3,3″); 8.58, **1**, *t*, H(4′); 8.35, **2**, *td*, H(4,4″); 7.87, **2**, *dd*, H(5,5″)[n]
(**8**) $[InMe_2(Et_3terpy)]NO_3$[l]	53.5 (52.7)	5.8 (5.8)	11.1 (10.7)	53	−0.16,**6**	8.72, **2**, *s*, H(3′5′); 8.71, **2**, *d*, H(6,6″); 8.63, **2**, *s*, H(3,3″); 7.72, **2**, *d*, H(5,5″); 3.09, **2**, *q*, CH$_2$′; 2.96, **4**, *q*, CH$_2$,CH$_2$″; 1.50, **3**, *t*, CH$_3$′; 1.41, **6**, *t*, CH$_3$,CH$_3$″[o]
(**9**) $[InMe_2(pymim)]NO_3$	36.5 (36.1)	4.1 (4.1)	15.5 (15.3)	76	−0.14,**6**	8.70, **1**, *d* (*br*), H(6); 8.18—8.14, **2**, *m*, H(3,4); 7.62, **1**, *m*, H(5); 7.45, **1**, *s*, and 7.22, **1** *s*, H(4′,5′); 4.16, **3**, *s*, CH$_3$
(**10**) $[(InMe)_2\{(py)_2(Ph)CO\}_2(NO_3)(H_2O)]NO_3 \cdot 0.75H_2O$[p]	46.0 (46.1)	3.6 (3.8)	8.3 (9.0)	130	−0.39,**6**[q]	8.02, *ca.* **4**, *br*; 7.46—7.36, *ca.* **18**, *m* (*br*); 7.24—7.22, *ca.* **4**, *m* (*br*)[q]
(**11**) $[(InMe)_2\{(py)_3CO\}_2(NO_3)(H_2O)]NO_3 \cdot 4H_2O$[r]	41.7 (41.7)	3.4 (2.5)	11.1 (11.4)	146	−0.36,**6**[s]	8.14, **6**, *br*, H(6); 7.95, **6**, *br*, H(4); 7.75, **6**, *br*, H(3); 7.38, **6**, *br*, H(5)[s]
(**12**) $[(InMe)_2\{(mim)_3CO\}_2(NO_3)(H_2O)]NO_3 \cdot 2H_2O$[t]	33.9 (34.3)	4.4 (4.3)	20.3 (20.0)	171	−0.14,**6**[u]	7.46, **2**, *s*, 7.44, **2**, *s*, 7.32, **2**, *s*, 7.00, **2**, *s*, 6.96, **2**, *s*, and 6.48, **2**, *s*, H(4,5); 3.63, **6**, *s*, NCH$_3$; *ca.* 3.33, NCH$_3$ and CD$_3$OD; 3.13, **6**, *s*, NCH$_3$[u]
(**13**) $[(InMe)_2\{(py)(mim)_2CO\}_2(NO_3)(H_2O)]NO_3 \cdot H_2O \cdot Me_2CO$[v]	38.0 (39.1)	4.2 (4.4)	16.4 (16.6)	134	0.04, *ca.* 1.5 −0.24, *ca.* 3 −0.37, *ca.* 1.5[w]	9—6, *ca.* **16**, *br resonances*; 3.62, *ca.* **3**, *s*, NCH$_3$; *ca.* 3.33, NCH$_3$ and CD$_3$OD; 2.18, *s*, Me$_2$CO[w]
(**14**) $[(InMe)_2\{(py)_2(mim)CO\}_2(NO_3)(H_2O)]NO_3 \cdot H_2O$[x]	40.3 (40.4)	4.1 (3.8)	14.7 (14.7)	116	*ca.* −0.3,**6**,*vbr*[y]	8.5—6.5, *ca.* **20**, *br resonances*; 3.46, **6**, *br*, NCH$_3$[y]

[a] Calculated values are given in parentheses. [b] For *ca.* 10^{-3} mol dm^{-3} solutions in methanol. [c] Shifts are in p.p.m. from SiMe$_4$ in CD$_3$OD; given as chemical shift, **relative intensity**, *multiplicity*, assignment. [d] Pale yellow. [e] $J(H^3,H^4) = 8.2$, $J(H^2,H^3) = 4.8$, and $J(H^2,H^4) = 1.5$ Hz. [f] $J(H^3,H^4) = 7.24$, $J(H^5,H^6) = 5.2$, $J(H^3,H^5) = 1.8$, $J(H^4,H^6)$ *ca.* 1.5, and $J(H^3,H^6)$ *ca.* 0.7 Hz. [g] $J(H^5,H^6)$ *ca.* 5 Hz. [h] $J(H^5,H^6) = 5.40$, $J(H^3,H^5) = 1.55$, and $J(CH_2,CH_3) = 7.6$ Hz. [i] ν(H$_2$O) 3 560m (br) and 3 430m (br) cm^{-1}. [j] $J(H^3,H^4) = 7.9$, $J(H^4,H^5)$ *ca.* 7.7, $J(H^5,H^6)$ *ca.* 5.2, and $J(H^4,H^6)$ *ca.* 1.8 Hz. [k] ν(OH) 3 224m (vbr) cm^{-1}. [l] Pale yellow when stored in darkness. [m] ν(H$_2$O) 3 530m (br) and 3 450m (br) cm^{-1}. [n] $J(H^3,H^4; H^4,H^5; H^{3'},H^{4'}; H^{4'},H^{5'})$ *ca.* 8, $J(H^5,H^6) = 5.4$, and $J(H^4,H^6) = 1.4$ Hz. [o] $J(CH_2,CH_3) = 7.60$ and $J(H^5,H^6)$ *ca.* 5.3 Hz. [p] ν(H$_2$O) 3 380m (vbr) cm^{-1}. [q] At −40 °C: −0.41, **6**, *s*, CH$_3$; 8.82, **2**, *d* (*br*); 8.28, **2**, '*t*' (*br*); 7.89, **2**, 't' (br); 7.81, **2**, '*t*' (*br*); 7.59, **2**, *m* (*br*); 7.5—7.3, **14**, *m*; 7.82, **2**, *m*, '*t*' (*br*). [r] ν(H$_2$O) 3 370m (vbr) cm^{-1}. [s] See Figure 3. At +50 °C: −0.26, **6**, *s*, InCH$_3$; 8.15, **6**, *br*, H(6); 7.94, **6**, '*t*' (*br*), H(4); 7.72, **6**, *d*, H(3), $J(H^3,H^4)$ *ca.* 7.9 Hz, 7.37, **6**, *m*, H(5). At −40 °C: −0.42, **6**, *s*, InCH$_3$; 8.79, **2**, *br*; 8.49, **2**, *br*; 8.25, **2**, *br*; 7.93, **4**, *br*; 7.85, **4**, *br*; 7.70, **2**, *br*; 7.57, **2**, *br*; 7.40, **2**, *br*; 7.13, **2**, *br*; 6.88, **2**, *br*. [t] ν(H$_2$O) 3 430m (vbr) cm^{-1}. [u] Unaltered at −40 °C. A spectrum obtained in D$_2$O confirmed that the complex exhibits three NCH$_3$ resonances, with one of these coincident with CD$_3$OD solvent. [v] ν(H$_2$O) 3 365m (vbr) cm^{-1}. [w] At −40 °C: 0.04, *ca.* **2**, *s*, −0.32, *ca.* **2**, *s*, and −0.48, *ca.* **2**, *s*, InCH$_3$; complex resonances at 8.96, 8.25—6.63, and 5.89 (py) and H(4,5)(mim); 3.62, *ca.* **5**, *s*, 3.54, *ca.* **1**, *s*, 3.33, with CD$_3$OD, and 3.20, *ca.* **1**, *s*, NCH$_3$. A spectrum in D$_2$O exhibits similar resonances in the NCH$_3$ region to that of the complex in CD$_3$OD at −40 °C, with four resonances in the ratio *ca.* 5:1:5:1. [x] ν(H$_2$O) 3 400m (vbr) cm^{-1}. [y] At −40 °C: 0.20, *ca.* **0.4**, 0.18, *ca.* **1.5**, −0.12, *ca.* **0.3**, −0.27, *ca.* **0.2**, −0.32, *ca.* **1.6**, −0.42, *ca.* **1.6**, and −0.52, *ca.* **0.4**, InCH$_3$; complex multiplets at 8.9—6.9, 6.62, 5.72 (py) and H(4,5) (mim); and sharp singlets at 3.57, *ca.* **2**, 3.56, *ca.* **2**, 3.48, *ca.* **2**, NCH$_3$.

weakly co-ordinated and ionic nitrate in $[InMe_2\{(py)_2CH_2\text{-}N,N'\}(NO_3\text{-}O)(H_2O)]$ and $[InMe_2(Et_3terpy\text{-}N,N',N'')]NO_3 \cdot H_2O$, respectively. Extension of this approach to the related methanols $(py)_2(Ph)COH$ and $(py)_n(mim)_{3-n}COH$ (n = 0—3) resulted in the isolation of a series of binuclear monomethylindium(III) complexes containing alkoxide bridges, *e.g.* $[InMe(H_2O)\{\mu\text{-}(py)_2(Ph)CO\text{-}N,N',\mu\text{-}O\}_2InMe(NO_3)]NO_3 \cdot 0.75H_2O$. A preliminary communication of part of this latter work has been published.[14]

Table 2. Co-ordination geometry for the indium atom in the dimethylindium(III) complexes $[InMe_2\{(py)_2CH_2\}(NO_3)(H_2O)]$ (**5**) and $[InMe_2(Et_3terpy)]NO_3$ (**8**) (distances in Å, angles in °)

Complex (**5**)		Complex (**8**)	
Atoms[a]		Atoms[b]	
In–C(A,B)	2.122(5), 2.128(6)	In–C(A,B)	2.131(8), 2.119(7)
In–N(a1,b1)	2.439(4), 2.424(4)	In–N(a1,b1,c1)	2.360(5), 2.310(5), 2.360(6)
In–O,O(1)	2.679(5), 2 632(4)		
In•••O(2)	3.077(4)		
C(A)–In–C(B)	157.6(2)	C(A)–In–C(B)	132.8(3)
C(A)–In–N(a1,b1)	95.2(2), 105.9(2)	C(A)–In–N(a1,b1,c1)	96.9(3), 111.7(3), 100.0(3)
C(B)–In–N(a1,b1)	98.2(2), 94.8(2)	C(B)–In–N(a1,b1,c1)	99.0(3), 115.4(3), 96.3(3)
N(a1)–In–N(b1)	76.0(1)	N(a1)–In–N(b1,c1)	69.3(2), 138.8(2)
In–N(a1)–C(a2,a6)	122.8(3), 118.4(3)	In–N(a1)–C(a2,a6)	118.6(4), 122.9(5)
In–N(b1)–C(b2,b6)	123.6(3), 117.2(3)	In–N(b1)–C(b2,b6)	120.2(4), 119.8(4)
In–O(1)–N	107.3(3)	In–N(c1)–C(c2,c6)	124.0(5), 118.1(4)
C(A)–In–O,O(1)	81.6(2), 84.3(2)	N(b1)–In–N(c1)	69.6(2)
C(B)–In–O,O(1)	81.2(2), 93.3(2)		
O–In–N(a1,b1)	87.3(1), 162.1(1)		
O–In–O(1)	123.6(1)		
O(1)–In–N(a1,b1)	148.4(1), 73.8(1)		
Deviation of atoms from mean planes			
$InC_2N_2O_2$ plane[c]		InN_3 plane[d]	
In	−0.001	In	0.000
N(a1,b1)	0.190, −0.137	N(a1,b1,c1)	−0.038, 0.023, −0.034
O,O(1)	−0.083, 0.132		
Deviation of In from the co-ordinated C_5N planes[e,f]			
Ring a,b	0.028, 0.216	Ring a,b,c	0.257, 0.102, 0.321

[a] The co-ordinated nitrate group in (**5**) has N–O(1,2,3,) 1.252(5), 1.230(6), 1.225(6) Å with angles opposite O(1,2,3) 121.3(4), 118.7(4), 120.0(4)°. The nitrate group is planar ($\chi^2 = 0.002$) and forms a dihedral angle of 22.9° with the InN_2O_2 mean plane. [b] The ionic nitrate group in (**8**) is planar ($\chi^2 = 0.604$), and has N–O(1,2,3) 1.23(1), 1.21(1), 1.19(1) Å with angles opposite O(1,2,3) 119.1(8), 121.5(8), 119.4(8)°. [c] For complex (**5**) the InN_2O_2 mean plane has $\chi^2 = 3\ 193$, and forms a dihedral angle of 88.6° with the InC_2 plane. [d] For complex (**8**) the InN_3 mean plane has $\chi^2 = 60.4$, and forms a dihedral angle of 88.3° with the InC_2 plane. [e] For complex (**5**) the C_5N mean planes (a,b) have $\chi^2 = 7.4$, 2.1 and form dihedral angles of 34.0, 44.8° with the InN_2O_2 mean plane. [f] For complex (**8**) the C_5N mean planes (a,b,c) have $\chi^2 = 0.7$, 5.4, 12.8 and form dihedral angles of 6.4, 3.4, 8.5° with the InN_3 mean planes. Dihedral angles formed between the C_5N mean planes are 3.1 (a,b), 8.3 (b,c), and 8.7° (a,c).

Results and Discussion

The dimethylindium(III) complexes (**1**)—(**9**), prepared from methanol solutions of $[InMe_2]NO_3$ and ligands in equimolar ratio, have appropriate microanalyses (C,H,N), conductivities, and ^1H n.m.r. spectra for formulation as 1:1 complexes $[InMe_2L]NO_3$ [L = phen (**1**), bipy (**2**), Me_2bipy (**3**), Et_2bipy (**4**), $(mim)_2CHOH$ (**6**), Et_3terpy (**8**), and pymim (**9**)], with hydrate formation indicated for the $(py)_2CH_2$ (**5**) and terpy (**7**) complexes (Table 1). N.m.r. spectra exhibit a single $InMe_2$ resonance at 0.04 to −0.16 p.p.m., with resonances of donor ring protons shifted *ca.* 0.05 to 0.7 p.p.m. downfield from free ligand values.

The monomethylindium(III) complexes (**10**)—(**14**) were prepared and characterized similarly (Table 1). For these complexes n.m.r. spectra are very complex, and are discussed together with other characterization data after presentation of results of the *X*-ray crystallographic studies for (**10**) and (**13**).

Structures of the Dimethylindium(III) *Complexes.*—Crystals suitable for structural studies could only be obtained for the $(py)_2CH_2$ and Et_3terpy complexes. These complexes have the ligands co-ordinated as bidentate and tridentate ligands (Figure 1), respectively, with In–N bond distances 2.310(5)—2.439(4) Å (Table 2), and weakly co-ordinated water [2.679(5) Å] and nitrate [2.632(4) Å] groups in the $(py)_2CH_2$ complex, to give the formulations $[InMe_2\{(py)_2CH_2\text{-}N,N'\}(NO_3\text{-}O)(H_2O)]$ and $[InMe_2(Et_3terpy\text{-}N,N',N'')]NO_3$. The projections in Figure 1(*a*) and (*b*) allow direct comparison with related dimethylthallium(III) complexes shown in ref. 12, and Figure 1(*c*) illustrates the five-co-ordinate geometry and bending of the InC_2 group in the Et_3terpy complex.

The nitrate groups are regular (bond lengths and angles within *ca.* 3σ), and the nitrate and pyridine rings are planar in both complexes (Table 1), with dihedral angles between rings (a,b) and (b,c) in Et_3terpy of 3.1 and 8.3°, respectively, similar to those found for $[(TlMe_2)_3(Et_3terpy)_2(NO_3)_3]$ (3.1, 2.5°),[12] but much less than those found for $[TlMe_2(terpy\text{-}N,N',N'')(H_2O)]NO_3$ (17.2, 18.0°),[12] and $[HgMe(Et_3terpy\text{-}N,N',N'')]NO_3$ (15.4, 18.6°).[15] The $(py)_2CH_2$ complex has the nitrogen and oxygen donor atoms in an 'equatorial plane' (InN_2O_2), with atom deviations from this plane ranging from −0.137 Å [N(b1)] to 0.190 Å [N(a1)]. The indium atoms lie close to the projected mean planes of the donor rings, with the maximum deviation (0.321 Å) occurring for ring c of the Et_3terpy complex. The $InMe_2$ groups form C(A)–In–C(B) angles of 157.6(2)° for the $(py)_2CH_2$ complex and 132.8(3)° for the Et_3terpy complex, with the difference presumably arising from the presence of three nitrogen donor groups in the latter and a more symmetrical array of donor atoms in the equatorial plane of the former complex.

The analogous $TlMe_2$ complexes have quite different structures, with $(py)_2CH_2$ forming a dimeric complex, [{Tl-

Table 3. Co-ordination geometry for the indium atoms in the methylindium(III) complexes $[(InMe)_2\{(py)_2(Ph)CO\}_2(NO_3)(H_2O)]NO_3{\cdot}0.75H_2O$ (**10**) and $[(InMe)_2\{(py)(mim)_2CO\}_2(NO_3)(H_2O)]NO_3{\cdot}H_2O{\cdot}Me_2CO$ (**13**) (distances in Å, angles in °)

Atoms[a]	Complex (**10**)	Complex (**13**)
In(1)–C(1)	2.140(11)	2.119(11)
In(1)–N(1a1,2c1)	2.409(9), 2 317(9)	2.391(7), 2.259(8)
In(1)–O(10,20,11)	2.208(6), 2.165(6), 2.422(12)	2.193(6), 2.233(6), 2.387(7)
In(1) • • • O(13)	2.692(15)	2.802(9)
In(1) • • • In(2)	3.494(1)	3.569(2)
O(10) • • • O(20)	2.607(8)	2.655(8)
C(1)–In(1)–N(1a1,2c1)	94.0(5), 101.8(4)	97.3(3), 106.0(4)
C(1)–In(1)–O(10,20,11)	116.4(4), 169.2(4), 92.9(5)	113.1(3), 169.1(3), 94.0(3)
N(1a1)–In(1)–N(2c1)	88.5(3)	87.1(3)
N(1a1)–In(1)–O(10,20,11)	69.2(3), 94.2(3), 150.6(3)	70.5(2), 93.0(2), 148.1(2)
N(2c1)–In(1)–O(10,20,11)	136.3(3), 71.5(3), 117.9(3)	136.6(2), 70.9(2), 118.2(3)
O(10)–In(1)–O(20,11)	73.2(3), 82.1(3)	73.7(2), 77.6(2)
O(20)–In(1)–O(11)	83.3(3)	78.9(2)
In(1)–N(1a1)–C(1a2,1a6)	114.0(7), 127.2(7)	115.2(5), 125.6(6)
In(1)–N(2c1)–C(2c2,2c6)	117.6(7), 124.8(7)	117.7(6), 135.8(7)
In(1)–O(11)–N(1)	101(1)	108.0(6)
In(1)–O(10)–In(2),C(10)	105.9(3), 115.3(6)	106.3(2), 116.5(5)
In(1)–O(20)–In(2),C(20)	107.2(2), 120.4(6)	107.1(2), 117.6(5)
In(2)–C(2)	2.160(13)	2.153(10)
In(2)–N(2a1,1c1)	2.360(10), 2.327(7)	2.334(7), 2.234(7)
In(2)–O(10,20,2)	2.170(6), 2.177(6), 2.304(9)	2.266(6), 2.204(6), 2.300(6)
C(2)–In(2)–N(2a1,1c1)	98.3(5), 100.5(4)	96.4(3), 104.3(3)
C(2)–In(2)–O(10,20,2)	163.4(5), 118.8(4), 91.3(5)	168.9(3), 114.8(3), 93.0(3)
N(2a1)–In(2)–N(1c1)	93.2(3)	88.5(3)
N(2a1)–In(2)–O(10,20,2)	96.3(3), 70.5(3), 160.1(3)	93.7(2), 72.0(2), 165.3(2)
N(1c1)–In(2)–O(10,20,2)	70.8(3), 138.8(3), 102.2(3)	71.3(2), 137.7(2), 100.1(3)
O(10)–In(2)–O(20,2)	73.7(2), 77.3(3)	72.9(2), 78.1(2)
O(20)–In(2)–O(2)	89.6(3)	93.8(2)
In(2)–N(2a1)–C(2a2,2a6)	115.0(7), 127.0(7)	115.5(5), 126.2(6)
In(2)–N(1c1)–C(1c2,1c6)	116.2(6), 123.6(7)	117.2(6), 135.5(6)
In(2)–O(10)–C(10)	120.3(6)	117.1(5)
In(2)–O(20)–C(20)	115.3(5)	114.7(5)
Deviations of atoms from the In_2O_2 mean planes[b]		
In(1,2)	0.002, 0.002	−0.005, −0.005
O(10,20)	−0.022, −0.020	0.028, 0.028
C(1,2)	−0.155, −0.364	−0.336, −0.325
N(1c1,2c1)	0.804, 0.978	0.815, 0.907
Deviations of In from the co-ordinated ring mean planes[c]		
In(1) • • • rings 1a,2c	0.059, 0.463	0.086, 0.162
In(2) • • • rings 2a,1c	0.131, 0.372	0.087, 0.115

[a] The co-ordinated nitrate groups have N(1)–O(11,12,13) 0.88(1), 1.42(2), 1.26(2) Å with angles opposite O(11,12,13) 102(1), 136(2), 122(1)° for (**10**) and 1.17(1), 1.24(1), 1.24(1) Å with angles 116.2(10), 120.1(9), 123.7(10)° for (**13**). The ionic nitrate groups have N(2)–O(21,22,23) 1.22(1), 1.21(1), 1.24(2) Å with angles opposite O(21,22,23) 114(1), 123(1), 123(1)° for (**10**) and 1.26(2), 1.26(2), 1.11(2) Å with angles 135(2), 125(2), 99(1)° for (**13**). [b] The planes have $\chi^2 = 12.5$ and 33.3, respectively. [c] For (**10**) the mean planes for rings 1a,2a,1c,2c have $\chi^2 = 0.4, 0.3, 7.1, 1.9$ and form dihedral angles of 84.5, 81.3, 11.1, 14.4° with the In_2O_2 mean plane. For (**13**) the mean planes for rings 1a,2a,1c,2c have $\chi^2 = 3.4, 7.2, 17.4, 10.6$ and form dihedral angles of 87.5, 81.7, 19.6, 20.4° with the In_2O_2 mean plane.

$Me_2[(py)_2CH_2$-*N*,*N*′$](NO_3$-*O*,μ-*O*′$)\}_2]$, and Et_3terpy forming a complex aggregate of composition $[(TlMe_2)_3(Et_3terpy)_2(NO_3)_3]$, although these structures are also characterized by weak M • • • O interactions and ionization in solution.[12] The most direct comparison is between $[InMe_2(Et_3$terpy-*N*,*N*′,*N*″$)]NO_3$ (**8**) and $[TlMe_2$(terpy-*N*,*N*′,*N*″$)]NO_3$, since these differ mainly in the presence of a weakly co-ordinated water molecule in the Tl complex [Tl–O 2.932(12) Å]. These two complexes have metal–carbon bond lengths within *ca.* 1σ (σ = 0.015 Å for Tl complex), but for indium the interaction with nitrogen donor ligands is clearly stronger, with In–N *ca.* 0.3 Å shorter. Consistent with this interpretation, the C(A)–In–C(B) angle in (**8**) is *ca.* 37° smaller than for the Tl complex, with both of these angles opposite the nitrogen donor ligand, although the angle for the Tl complex will be influenced by the more symmetrical distribution of Tl • • • N,O interactions in the equatorial plane.

Photochromism of (**7**) *and* (**8**).—The crystalline terpy and Et_3terpy complexes are pale yellow when stored in darkness, but became emerald green over *ca.* 30 min on exposure to strong light and revert to yellow over *ca.* 7 d when placed in darkness. Differences in absorption may result from electronic transitions within the ligand, perhaps resulting from changes in co-ordination mode, *e.g.* tridentate (yellow) ⟷ bidentate (green) for cations $[InMe_2L]^+$. Isomerizations of this type are probably

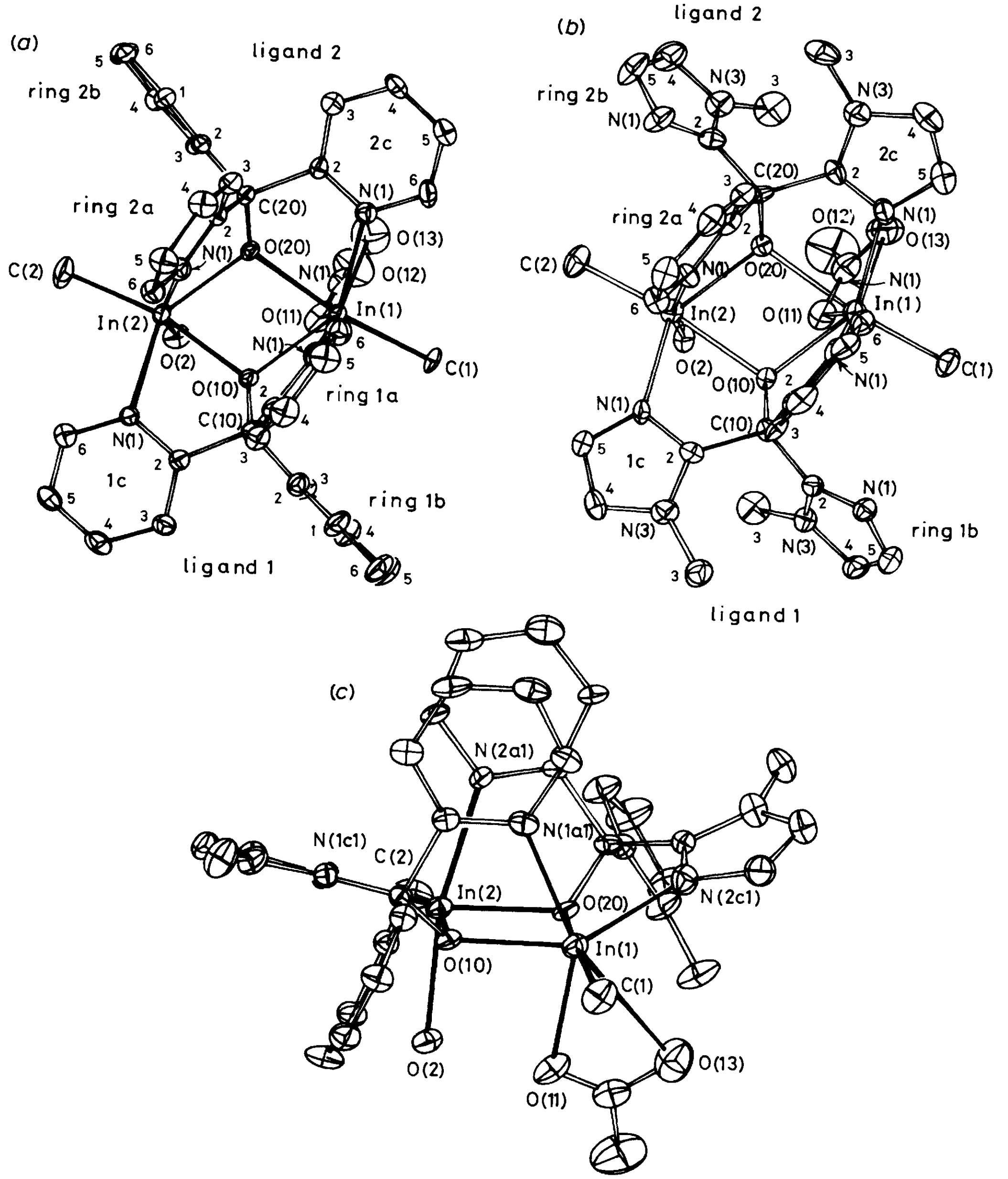


Figure 2. Structures of (*a*) $[(InMe)_2\{\mu\text{-}(py)_2(Ph)CO\text{-}N,N',\mu\text{-}O\}_2(NO_3)(H_2O)]^+$ in (**10**), (*b*) $[(InMe)_2\{\mu\text{-}(py)(mim)_2CO\text{-}N,N',\mu\text{-}O\}_2(NO_3)(H_2O)]^+$ in (**13**), with projections normal to the In_2O_2 group in each case, showing atom numbering with hydrogen atoms omitted to improve clarity, and (*c*) a different projection of the cation in (**13**) with atom numbering limited to the indium atoms and their immediate co-ordination sphere

confined to the surface of the crystals since the crystal clarity and shape are unaffected by repeated cycles.

Structures of the Monomethylindium(III) *Complexes*.—Crystals of (**10**) and (**13**) were found to contain the binuclear cations shown in Figure 2. For both structures the cations have inequivalent InMe groups bridged by two deprotonated ligands forming alkoxide bridges in an 'In_2O_2' kernel. In the $(py)_2(Ph)CO^-$ complex (**10**) the pyridine groups of each ligand are co-ordinated to each indium atom, so that the bridge may be represented as $\mu\text{-}(py)_2(Ph)CO\text{-}N,N',\mu\text{-}O$. The ligand $(py)(mim)_2CO^-$ behaves similarly in (**13**), with one py group co-ordinated to one indium atom, one mim group co-ordinated to the other indium atom, and one group unco-ordinated, such that each indium atom has one py and one mim group co-ordinated to it. For both cations six co-ordination of In(2), $InCN_2O_3$, is completed by a water molecule, and a nitrate group interacts unsymmetrically with In(1), so that the cations may be formulated as $[InMe(H_2O)\{\mu\text{-}(py)_2(Ph)CO\text{-}N,N',\mu\text{-}O\}_2InMe(NO_3)]^+$ in (**10**) and $[InMe(H_2O)\{\mu\text{-}(py)(mim)_2CO\text{-}N,N',\mu\text{-}O\}_2InMe(NO_3)]^+$ in (**13**). Mean planes calculated for the In_2O_2 kernels (Table 3) show that the maximum deviation from the planes is 0.028 Å [both O(10) and O(20) in (**13**)], with the methyl groups also close to these planes [maximum deviation −0.364 Å for C(2) in (**10**)], but the nitrogen donors N(1c1) and N(2c1) are further removed [0.804—0.978 Å], as illustrated for (**13**) in Figure 2(*c*). The methyl groups are *trans* to each other for an 'equatorial plane' through $In_2C_2O(10)O(20)N(1c1)$-N(2c1), and the pyridine donors N(2a1) and N(1a1) are 'axial' and *trans* to aqua [In(2)] and nitrate [In(1)] groups, respectively. The alkoxide bridges form the shortest In–O bonds, 2.165(6)—2.266(6) Å, compared with 2.422 (12) Å in (**10**) and 2.387(7) Å in (**13**) for aqua ligands, and the bridges are slightly unsymmetrical, with In–O bonds *trans* to methyl groups *ca.* 0.01—0.04 Å longer than those *trans* to py [(**10**)] or mim [(**13**)] groups. The nitrate groups form the weakest (semi-bidentate) co-ordination, with In(1)–O(11) 2.422(12) [(**10**)] and 2.387(7) Å [(**13**)], and In(1)···O(13) 2.692(15) [(**10**)] and 2.802(9) Å [(**13**)]. Indium–nitrogen distances in (**10**) and (**13**), 2.234(7)—2.409(9) Å, span a similar range to those found for the dimethylindium(III) complexes, 2.310(5)—2.439(4) Å, and the indium atoms lie close to the mean planes of py and mim donor groups (0.059—0.463 Å).

The geometry at the indium atoms in both structures is irregular, with bond angles at In(1) 69.2(3)—117.9(3) [(**10**)], 70.5(2)—118.2(3)° [(**13**)], and at In(2) 70.5(3)—118.8(4) [(**10**)], and 71.3(2)—114.8(3)° [(**13**)], where the angles quoted exclude *trans* donors and weakly interacting O(13). Except for the orientation of aqua and nitrate groups in each complex, the indium atoms have similar geometry, with analogous donor atoms of the other five groups subtending angles at indium within 6 [(**10**)] and 2° [(**13**)] of each other.

The average value for In–O bonds in (**10**) and (**13**) is 2.20 Å, similar to that for In–(μ-OH) [2.17(2) Å] and In–(μ_4-O) [2.12(2) Å] bonds in the [tris(trimethylsilyl)methyl] indium(III) complex [{In[C(SiMe$_3$)$_3$]}$_4$(μ_4-O)(μ-OH)$_6$],[16] which has hydroxo bridges between each pair of indium atoms oriented tetrahedrally around a central oxygen.

With the structures of (**10**) and (**13**) as a guide, the remaining monomethylindium(III) complexes may be similarly formulated (Table 1) with co-ordinated aqua and nitrate groups assumed, although other combinations appear to be feasible, *e.g.* two aqua groups with two ionic nitrates. The complexes are assumed to be formed *via* elimination of methane on reaction of the alcohols (py)$_2$(Ph)COH and (py)$_n$(mim)$_{3-n}$COH (n = 0—3) with dimethylindium(III), as a similar loss of methane occurs on reaction of methylindium(III) substrates with a range of reagents.[5,7,8,17] In particular, trimethylindium(III) forms the alkoxides [{InMe$_2$(μ-OMe)}$_3$] and [{InMe$_2$(μ-OCBu^t)}$_2$] on reaction with methanol[18,19] and t-butyl alcohol,[20] respectively, and forms the crystallographically characterized dimers [{InMe$_2$[μ-N(Me)R]}$_2$] (R = Me[21] or Ph[22]) on reaction with the appropriate amine. The co-ordination mode of the ligands is similar to that of the pyridin-2-ylmethanolato ligand in some organoaluminium(III) derivatives, *e.g.* [{AlBu$^i_2$(μ-pyCH$_2$O-*N*,μ-*O*)}$_2$], which are also formed *via* alkane elimination.[23]

The monomethylindium(III) derivatives provide the first examples of these types of tridentates as bridging ligands, [μ-(py)$_2$(Ph)CO-*N*,*N*′,μ-*O*]$^-$ and [μ-(py)$_n$(mim)$_{3-n}$CO-*N*,*N*′,μ-*O*]$^-$ (n = 0—3), with previous structural studies of mononuclear complexes revealing tridentate (py)$_3$COH-*N*,*N*′,*N*″ co-ordination for Hg^{II}Me[24] and Co^{III},[25,26] tridentate [(py)$_3$CO-*N*,*N*′,*O*]$^-$ co-ordination for Co^{III},[25] tridentate (py)$_n$(mim)$_{3-n}$COH-*N*,*N*′,*N*″ (n = 1[27] or 2[24]) co-ordination for Hg^{II}Me, bidentate (py)$_n$(mim)$_{3-n}$COH-*N*,*N*′ (n = 0[28] or 1[29]) co-ordination for Au^{III}Me$_2$, and unidentate (mim)$_3$COH-*N* co-ordination with an additional weak Hg···OH interaction for Hg^{II}Me.[30]

Solution Properties of the Binuclear Monomethylindium(III) *Complexes*.—Complex (**10**) exhibits a single InMe resonance (−0.39 p.p.m.) and broad (py)$_2$(Ph)CO$^-$ resonances in the ^{1}H n.m.r. spectrum at ambient temperature with integration indicating an InMe:(py)$_2$(Ph)CO ratio of 1:1 (Table 1), but at −40 °C the ligand resonances occur as multiplets in the ratio 2:2:2:2:2:14:2, consistent with the presence of two py environments. Similar results are obtained for the (py)$_3$CO$^-$ [(**11**)] and (mim)$_3$CO$^-$ [(**12**)] complexes, with three ring environments observed at low temperature for (**11**) (Figure 3) and at ambient temperature for (**12**), consistent with the presence of 'axial', 'equatorial', and unco-ordinated donor rings. For example, (**11**) exhibits a spectrum at −40 °C with a single InMe resonance (−0.42 p.p.m., 6 H) and ten ligand resonances in the ratio 2:2:2:4:4:2:2:2:2:2 (Figure 3). Thus, in contrast to the solid-state structures of (**10**) and (**13**), spectra of the monomethylindium(III) complexes in CD$_3$OD indicate presence of equivalent indium environments, as indicated in Figure 4, where the two-fold axis in the cations results from replacement of aqua and nitrate groups (in the solids) by solvent, aqua, or rapidly exchanging solvent and aqua groups, represented by S. 'Axial' and 'equatorial' donors are represented by N(a) and N(c), respectively, as in Figure 2(*c*) for crystalline (**13**).

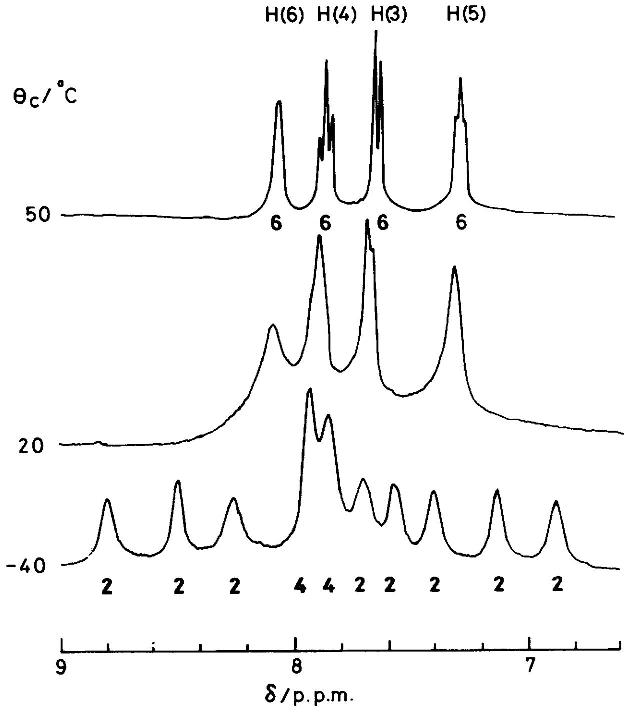


Figure 3. Variable-temperature ^{1}H n.m.r. spectra, in the region containing pyridin-2-yl resonances only, for [(InMe)$_2${(py)$_3$CO}$_2$-(NO$_3$)(H$_2$O)]NO$_3$·4H$_2$O (**11**) in CD$_3$OD. Relative intensities are given below the peaks, with assignment not attempted for the spectrum at −40 °C

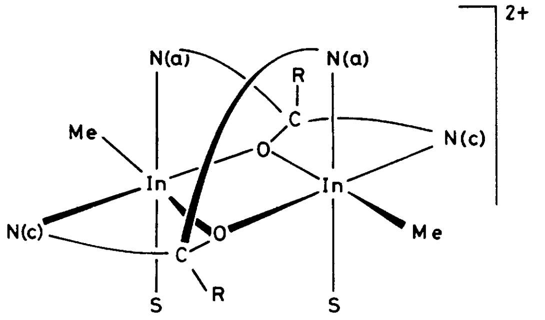


Figure 4. Proposed structures of the cations formed by (**10**)—(**14**) in solution

Consistent with dissociation of the co-ordinated nitrate group to form [(InMeL)$_2$]$^{2+}$·2NO$_3$$^-$, complexes (**10**)—(**14**) have molar conductances of 116—171 ohm^{-1} cm^2 mol^{-1}, higher than for the In^{III}Me$_2$ complexes, 53—93 ohm^{-1} cm^2 mol^{-1}, which are expected to form 1:1 electrolytes, $[InMe_2L]^+NO_3^-$ (Table 1).

The temperature dependence of the n.m.r. spectra for the $(py)_2(Ph)CO^-$, $(py)_3CO^-$, and $(mim)_3CO^-$ complexes is assumed to arise from rapid exchange between 'axial' and 'equatorial' environments, together with unco-ordinated ring environments for the ligands with three donor rings. For the complexes containing $(py)(mim)_2CO^-$ [(**13**)] and $(py)_2(mim)CO^-$ [(**14**)] as ligands, the spectra are very complex. At ambient temperature (**13**) exhibits three InMe resonances in *ca.* 1.5:3:1.5 ratio and broad ligand resonances, and at −40 °C the InMe resonances are sharper and the ligand resonances are present as many complex multiplets; at ambient temperature (**14**) exhibits a very broad InMe resonance and broad ligand resonances, but at −40 °C exhibits seven InMe resonances, three NMe proton resonances, and complex multiplets for aromatic protons (Table 1). The complexity of the spectra for (**13**) and (**14**) is assumed to result from the presence of exchange between structural isomers, in addition to exchange between 'axial', 'equatorial', and unco-ordinated rings within each isomer. From Figure 4 it is apparent that for ligands of formula N_2RCO^- and N_3CO^- only one isomer is possible, as observed in low-temperature spectra of the $(py)_2(Ph)CO^-$, $(py)_3CO^-$, and $(mim)_3CO^-$ complex, but for $N_2(N')CO^-$ six isomers may be readily drawn. These isomers, (**I**)—(**VI**), may be represented by In*N*′(*a*)N(c)·InN′(a)*N*(*c*) (**I**), In*N*(*a*)N′(c)·InN(a)*N*′(*c*) (**II**), In*N*(*a*)N(c)·InN(a)*N*(*c*) (**III**), In*N*(*a*)N(c)·InN′(a)*N*′(*c*) (**IV**), In*N*(*a*)N(c)·InN(a)*N*′(*c*) (**V**), and In*N*′(*a*)N(c)·InN(a)*N*(*c*) (**VI**), where italicized nitrogens belong to the same ligand, *N*$_2$(*N*′)*CO*$^-$. Three of these isomers, (**I**)—(**III**), have equivalent indium environments within each cation, *e.g.* both indium atoms in (**I**) have InMe(S)N′(a)N(c)(μ-O)$_2$ environments, with this arrangement occurring in the solid state for (**13**) [Figure 2(*b*) and (*c*), In*py*(*a*)mim(c)·Inpy(a)*mim*(*c*) with co-ordinated aqua and nitrate groups instead of S], and the others (**IV**)—(**VI**) have inequivalent indium environments, giving nine possible InMe environments. Thus, for complexes

Table 4. Specific crystallographic details

Complex	$[InMe_2\{(py)_2CH_2\}(NO_3)(H_2O)]$ (**5**)	$[InMe_2(Et_3terpy)]NO_3$ (**8**)	$[(InMe)_2\{(py)_2(Ph)CO\}_2(NO_3)(H_2O)]NO_3\cdot0.75H_2O$ (**10**)	$[(InMe)_2\{(py)(mim)_2CO\}_2(NO_3)(H_2O)]NO_3\cdot H_2O\cdot Me_2CO$ (**13**)
Formula	$C_{13}H_{18}InN_3O_4$	$C_{23}H_{29}InN_4O_3$	$C_{36}H_{34}In_2N_6O_9\cdot0.75H_2O$	$C_{33}H_{44}In_2N_{12}O_{11}$
M	395.1	524.3	937.9	1 014.4
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	*P*2$_1$/*c*, no. 14	*P*2$_1$/*c*, no. 14	*P*$\bar{1}$, no. 2	*P*2$_1$/*c*, no. 14
a/Å	9.002(3)	8.641(3)	19.147(5)	14.388(6)
b/Å	12.538(7)	15.872(6)	11.007(4)	17.613(10)
c/Å	13.996(7)	17.242(7)	9.486(8)	16.403(10)
β/°	91.26(3)	90.78(3)	88.79(6)*	92.18(3)
U/Å^3	1 579(1)	2 365(2)	1 940(2)	4 154(2)
D_c/g cm^{-3}	1.66	1.47	1.61	1.62
Z	4	4	2	4
F(000)	792	1 072	469.5	2 048
μ_{Mo}/cm^{-1}	14.2	9.6	11.7	11.1
Specimen size (mm)	0.30 × 0.20 × 0.25	0.40 × 0.12 × 0.16	0.12 × 0.10 × 0.33	0.14 × 0.16 × 0.18
Absorption factor (min., max.)	1.22, 1.33	1.12, 1.18	1.13, 1.17	1.07, 1.11
$2\theta_{max.}$/°	50	50	50	50
N	2 796	4 192	6 428	7 165
N_o	2 155	2 502	4 486	3 676
R	0.033	0.047	0.064	0.052
R′	0.039	0.047	0.085	0.045

* α = 76.14(6)°, γ = 87.87(3)°.

Table 5. Non-hydrogen atomic co-ordinates for $[InMe_2\{(py)_2CH_2\}(NO_3)(H_2O)]$ (**5**)

Feature	Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
InMe$_2$	In	0.399 97(3)	0.229 71(3)	0.147 40(2)	C(B)	0.526 6(6)	0.153 2(5)	0.040 6(4)
	C(A)	0.357 0(6)	0.331 3(4)	0.264 9(4)				
(py)$_2$CH$_2$	N(a1)	0.205 0(4)	0.304 1(3)	0.043 6(3)	C(b2)	0.060 1(5)	0.118 3(4)	0.144 5(3)
	C(a2)	0.059 0(5)	0.293 8(4)	0.061 8(3)	C(b3)	−0.044 5(6)	0.037 9(5)	0.135 5(4)
	C(a3)	−0.046 3(5)	0.336 3(4)	−0.001 1(4)	C(b4)	0.000 3(7)	−0.066 6(5)	0.130 3(4)
	C(a4)	−0.004 1(6)	0.390 1(5)	−0.081 4(4)	C(b5)	0.149 9(6)	−0.089 6(4)	0.134 0(4)
	C(a5)	0.144 5(6)	0.402 1(4)	−0.097 9(4)	C(b6)	0.249 0(5)	−0.006 4(4)	0.143 2(3)
	C(a6)	0.244 5(5)	0.356 6(4)	−0.034 4(3)	C(7)	0.017 6(5)	0.233 4(4)	0.149 1(4)
	N(b1)	0.206 4(4)	0.095 4(3)	0.147 5(3)				
Nitrate	N	0.599 9(5)	0.121 0(4)	0.315 6(3)	O(2)	0.679 2(5)	0.182 3(4)	0.270 9(3)
	O(1)	0.478 3(4)	0.090 7(3)	0.280 1(3)	O(3)	0.637 4(5)	0.088 5(4)	0.395 1(3)
Water	O	0.569 4(6)	0.395 1(4)	0.096 9(3)				

(13) and **(14)**, complex spectra are expected, where some or all of the possible isomers may be present in unequal amounts, where the rates of exchange between isomers and between environments within each isomer may differ, and where possible coincidence of resonances may occur.

Experimental

Dimethylindium(III) iodide,[31,32] 4,4′-diethyl-2,2′-bipyridyl (Et_2bipy),[33] bis(pyridin-2-yl)methane [$(py)_2CH_2$],[34] 4,4′,4″-triethyl-2,2′:6′,2″-terpyridyl (Et_3terpy),[35] *N*-methyl-2-(pyridin-2-yl)imidazole (pymim),[15] bis(*N*-methylimidazol-2-yl)methanol

Table 6. Non-hydrogen atomic co-ordinates for $[InMe_2(Et_3terpy)]NO_3$ (**8**)

Feature	Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
$InMe_2$	In	0.389 46(6)	0.210 20(3)	1.005 38(3)	C(B)	0.308 9(10)	0.085 6(5)	0.986 7(5)
	C(A)	0.466 9(9)	0.275 9(5)	1.106 5(4)				
Et_3terpy	N(a1)	0.153 3(6)	0.283 1(4)	0.988 8(3)	C(b41)	0.419 3(11)	0.460 9(6)	0.702 6(5)
	C(a2)	0.141 8(8)	0.340 3(5)	0.932 6(4)	C(b42)	0.500 2(14)	0.539 5(7)	0.722 7(6)
	C(a3)	0.013 0(9)	0.391 9(5)	0.924 9(5)	C(b5)	0.280 3(9)	0.398 7(5)	0.815 7(4)
	C(a4)	−0.108 0(9)	0.381 9(6)	0.978 8(6)	C(b6)	0.275 9(8)	0.345 0(4)	0.879 7(4)
	C(a41)	−0.260 9(16)	0.436 6(7)	0.980 5(7)	N(c1)	0.626 8(6)	0.193 7(3)	0.940 9(3)
	C(a42)	−0.255 9(11)	0.494 6(8)	0.921 7(7)	C(c2)	0.736 6(8)	0.139 2(5)	0.962 6(4)
	C(a5)	−0.093 0(10)	0.322 7(6)	1.034 5(5)	C(c3)	0.861 3(9)	0.119 8(5)	0.918 0(5)
	C(a6)	0.036 5(9)	0.275 5(5)	1.037 5(5)	C(c4)	0.883 5(10)	0.161 5(6)	0.850 4(6)
	N(b1)	0.395 5(6)	0.294 8(3)	0.896 5(3)	C(c41)	1.017 5(16)	0.140 1(10)	0.799 6(10)
	C(b2)	0.520 4(7)	0.294 9(4)	0.851 1(4)	C(c42)	1.053 4(26)	0.164 3(15)	0.746 0(12)
	C(b3)	0.530 9(8)	0.348 3(5)	0.788 6(4)	C(c5)	0.773 2(9)	0.220 6(5)	0.828 0(4)
	C(b4)	0.408 7(9)	0.401 0(5)	0.769 8(4)	C(c6)	0.646 1(8)	0.235 0(4)	0.873 5(4)
Nitrate	N	0.914 0(9)	0.109 0(5)	0.179 5(5)	O(2)	0.902 7(8)	0.081 3(5)	0.244 6(4)
	O(1)	0.816 7(8)	0.159 5(5)	0.155 1(4)	O(3)	1.021 1(10)	0.087 8(5)	0.141 0(5)

Table 7. Non-hydrogen atomic co-ordinates for $[(InMe)_2\{(py)_2(Ph)CO\}_2(NO_3)(H_2O)]NO_3\cdot0.75H_2O$ (**10**)

Feature	Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
InMe	In(1)	0.330 17(3)	−0.040 17(6)	0.361 57(8)	In(2)	0.156 48(3)	0.008 57(6)	0.250 04(8)
	C(1)	0.439 9(6)	−0.010 6(15)	0.331 7(16)	C(2)	0.050 1(6)	−0.047 2(13)	0.240 2(18)
Ligand 1	N(1a1)	0.304 3(4)	0.162 9(8)	0.407 6(10)	C(1b5)	0.461 6(8)	0.246 8(17)	−0.108 2(19)
	C(1a2)	0.279 5(5)	0.249 0(9)	0.290 8(11)	C(1b6)	0.443 6(8)	0.330 9(15)	−0.026 6(21)
	C(1a3)	0.263 9(7)	0.370 9(10)	0.300 9(15)	N(1c1)	0.149 6(4)	0.210 5(7)	0.102 3(9)
	C(1a4)	0.274 3(8)	0.403 4(12)	0.430 8(13)	C(1c2)	0.210 2(5)	0.266 8(9)	0.066 8(11)
	C(1a5)	0.298 3(8)	0.317 1(13)	0.549 0(15)	C(1c3)	0.212 8(6)	0.376 0(10)	−0.041 2(12)
	C(1a6)	0.312 6(7)	0.196 1(12)	0.527 7(15)	C(1c4)	0.152 1(7)	0.428 9(10)	−0.104 0(13)
	C(1b1)	0.384 9(7)	0.317 6(12)	0.060 4(16)	C(1c5)	0.090 7(6)	0.373 9(10)	−0.065 1(12)
	C(1b2)	0.340 3(6)	0.223 6(10)	0.058 1(14)	C(1c6)	0.090 4(6)	0.263 7(10)	0.035 5(11)
	C(1b3)	0.357 0(6)	0.140 4(12)	−0.026 3(13)	C(10)	0.273 8(5)	0.201 2(9)	0.154 5(12)
	C(1b4)	0.417 0(7)	0.152 9(16)	−0.111 1(18)	O(10)	0.261 3(3)	0.073 3(6)	0.192 5(8)
Ligand 2	N(2a1)	0.146 4(4)	0.079 3(7)	0.465 9(10)	C(2b5)	0.047 7(6)	−0.415 6(10)	0.607 2(12)
	C(2a2)	0.168 7(5)	−0.002 9(8)	0.585 3(11)	C(2b6)	0.043 0(6)	−0.331 4(10)	0.691 6(13)
	C(2a3)	0.162 5(6)	0.021 4(9)	0.718 4(14)	N(2c1)	0.322 3(5)	−0.125 3(8)	0.609 4(10)
	C(2a4)	0.133 5(7)	0.134 4(11)	0.734 4(14)	C(2c2)	0.261 9(5)	−0.171 1(9)	0.662 5(11)
	C(2a5)	0.110 7(7)	0.220 4(10)	0.610 1(14)	C(2c3)	0.254 2(6)	−0.246 6(10)	0.800 0(12)
	C(2a6)	0.118 0(6)	0.190 0(10)	0.481 0(14)	C(2c4)	0.310 8(7)	−0.272 1(12)	0.888 5(14)
	C(2b1)	0.090 2(5)	−0.236 7(9)	0.678 4(11)	C(2c5)	0.373 4(7)	−0.222 9(14)	0.836 3(15)
	C(2b2)	0.144 3(5)	−0.228 0(8)	0.577 4(10)	C(2c6)	0.377 8(6)	−0.152 0(13)	0.700 6(13)
	C(2b3)	0.149 8(5)	−0.313 8(9)	0.493 8(11)	C(20)	0.199 8(5)	−0.127 8(8)	0.556 0(10)
	C(2b4)	0.101 6(6)	−0.407 9(10)	0.508 3(12)	O(20)	0.225 3(3)	−0.105 2(6)	0.413 4(7)
Co-ordinated nitrate	N(1)	0.341 9(5)	−0.253 3(9)	0.262 6(9)	O(12)	0.360 6(8)	−0.362 8(13)	0.214 0(16)
	O(11)	0.330 6(5)	−0.182 1(10)	0.201 9(11)	O(13)	0.354 4(8)	−0.288 0(13)	0.396 0(18)
Ionic nitrate	N(2)	0.115 8(6)	0.620 5(9)	0.124 2(12)	O(22)	0.178 0(5)	0.628 1(9)	0.136 3(13)
	O(21)	0.084 1(6)	0.526 5(10)	0.179 5(13)	O(23)	0.086 3(7)	0.717 4(12)	0.053 7(17)
Co-ordinated water	O(2)	0.193 4(4)	−0.107 7(7)	0.088 7(8)				
Solvent water *	O(1)	0.482(3)	0.432(5)	0.495(7)	O(1″)	0.475(4)	0.500(7)	0.560(8)
	O(1′)	0.487(3)	0.379(6)	0.391(7)				

* Assigned site occupancies 0.25.

Table 8. Non-hydrogen atomic co-ordinates for $[(InMe)_2\{(py)(mim)_2CO\}_2(NO_3)(H_2O)]NO_3 \cdot H_2O \cdot Me_2CO$ **(13)**

Feature	Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
InMe	In(1)	0.391 87(5)	0.149 76(4)	0.195 45(4)	In(2)	0.196 11(5)	0.139 23(4)	0.322 19(4)
	C(1)	0.489 3(7)	0.215 9(7)	0.132 8(7)	C(2)	0.122 2(8)	0.084 9(6)	0.417 9(6)
Ligand 1	N(1a1)	0.270 5(5)	0.151 4(4)	0.091 8(4)	C(1b4)	0.336 4(7)	0.437 6(6)	0.155 8(6)
	C(1a2)	0.205 2(6)	0.202 5(5)	0.101 8(5)	C(1b5)	0.331 0(7)	0.411 1(6)	0.079 4(6)
	C(1a3)	0.129 7(7)	0.209 8(5)	0.047 9(5)	N(1c1)	0.100 1(5)	0.231 0(4)	0.277 1(4)
	C(1a4)	0.121 5(7)	0.159 8(6)	−0.016 2(6)	C(1c2)	0.126 9(7)	0.271 9(5)	0.215 6(5)
	C(1a5)	0.188 4(8)	0.106 0(6)	−0.026 5(6)	N(1c3)	0.063 7(5)	0.327 0(5)	0.198 7(5)
	C(1a6)	0.262 9(7)	0.103 9(6)	0.028 2(5)	C(1c3)	0.064 7(8)	0.388 7(7)	0.139 7(7)
	N(1b1)	0.289 3(5)	0.341 7(4)	0.073 7(4)	C(1c4)	−0.008 3(7)	0.317 9(6)	0.250 2(6)
	C(1b2)	0.269 5(6)	0.325 5(5)	0.150 4(5)	C(1c5)	0.014 6(7)	0.257 0(6)	0.297 3(6)
	N(1b3)	0.297 1(5)	0.381 2(4)	0.202 3(4)	C(10)	0.220 8(6)	0.255 9(5)	0.177 3(5)
	C(1b3)	0.285 7(8)	0.384 1(7)	0.289 5(6)	O(10)	0.274 1(4)	0.216 2(3)	0.237 8(3)
Ligand 2	N(2a1)	0.138 1(5)	0.062 2(4)	0.216 3(4)	C(2b4)	0.296 8(8)	−0.127 7(7)	0.420 5(7)
	C(2a2)	0.192 4(6)	0.006 8(5)	0.195 2(5)	C(2b5)	0.209 2(8)	−0.137 0(7)	0.388 9(7)
	C(2a3)	0.167 1(7)	−0.045 1(6)	0.134 5(5)	N(2c1)	0.417 8(5)	0.028 0(5)	0.159 4(5)
	C(2a4)	0.080 7(8)	−0.038 6(7)	0.096 5(6)	C(2c2)	0.365 2(6)	−0.023 7(5)	0.189 1(6)
	C(2a5)	0.021 8(7)	0.017 5(7)	0.121 3(6)	N(2c3)	0.391 7(6)	−0.093 6(5)	0.168 4(5)
	C(2a6)	0.053 4(6)	0.067 5(6)	0.179 0(6)	C(2c3)	0.355 9(9)	−0.168 2(6)	0.190 0(8)
	N(2b1)	0.192 6(6)	−0.093 2(5)	0.321 9(5)	C(2c4)	0.466 3(8)	−0.084 9(7)	0.118 4(7)
	C(2b2)	0.270 2(7)	−0.055 2(5)	0.313 5(6)	C(2c5)	0.483 2(7)	−0.009 6(7)	0.115 2(7)
	N(2b3)	0.336 0(5)	−0.073 2(5)	0.373 0(5)	C(20)	0.287 9(6)	0.000 1(5)	0.244 9(5)
	C(2b3)	0.429 7(8)	−0.047 0(8)	0.382 8(8)	O(20)	0.312 8(4)	0.072 8(3)	0.275 9(3)
Co-ordinated nitrate	N(1)	0.508 2(6)	0.151 0(6)	0.348 5(5)	O(12)	0.545 0(8)	0.152 2(8)	0.418 3(6)
	O(11)	0.446 9(5)	0.190 9(4)	0.327 2(4)	O(13)	0.538 2(6)	0.102 7(5)	0.301 2(6)
Ionic nitrate	N(2)	0.854 3(10)	0.205 2(7)	0.000 0(12)	O(22)	0.915 4(8)	0.252 9(7)	−0.017 6(7)
	O(21)	0.894 5(8)	0.174 7(7)	0.061 3(7)	O(23)	0.780 4(12)	0.196 0(9)	−0.018 8(10)
Co-ordinated water	O(2)	0.289 3(4)	0.207 2(4)	0.412 8(4)				
Solvent water	O(1)	0.715 0(10)	0.063 7(7)	0.075 1(8)				
Solvent acetone	C(1)	0.809 3(11)	0.103 4(8)	0.290 3(12)	C(12)	0.819 4(22)	0.099 4(14)	0.379 0(12)
	C(11)	0.766 4(13)	0.173 6(10)	0.253 0(15)	O(1)	0.820 1(10)	0.051 1(6)	0.240 0(8)

$[(mim)_2CHOH]$ and tris(*N*-methylimidazol-2-yl)methanol $[(mim)_3COH]$,[36,37] tris(pyridin-2-yl)methanol $[(py)_3COH]$,[38] bis(*N*-methylimidazol-2-yl)(pyridin-2-yl)methanol $[(py)(mim)_2\text{-}COH]$,[37,39] (*N*-methylimidazol-2-yl)bis(pyridin-2-yl)methanol $[(py)_2(mim)COH]$,[39] and phenylbis(pyridin-2-yl)methanol $[(py)_2(Ph)COH]$[38] were prepared as described. The remaining ligands were obtained commercially, and were used as received, except for 2,2′:6′,2″-terpyridyl which was recrystallized from methanol after sublimation at 90 °C.

Synthesis of Dimethylindium(III) *Complexes*.—The complexes were obtained in yields of 56—83%, except for the $(mim)_2COH$ complex (37%). In a typical synthesis, thallium(I) nitrate (0.116 g, 0.434 mmol) in water (*ca*. 1 cm^3) was added to dimethylindium(III) iodide (0.117 g, 0.432 mmol) in methanol (*ca*. 8 cm^3) with stirring, to give a yellow precipitate of TlI. The suspension was stirred for 4 h, filtered, and 1,10-phenanthroline (0.087 g, 0.437 mmol) in methanol (*ca*. 1 cm^3) added. On allowing the solvent to evaporate at ambient temperature clear crystals formed at low volume, which were collected. The crystals became opaque on drying. Recrystallization was not required prior to microanalysis, except for the terpy complex which was recrystallized from acetone with exposure of the acetone solution to diethyl ether in a closed chamber.

Synthesis of Monomethylindium(III) *Complexes*.—Following a similar procedure to that above, white plates were obtained from $(py)_3COH$ (87% yield) and $(py)_2(mim)COH$ (36%) as reagents, colourless crystals were obtained from $(py)_2(Ph)COH$ (74%), and, in slow evaporation to dryness, a white solid was obtained from $(mim)_3COH$ and a glassy solid from $(py)(mim)_2COH$. The products obtained from $(mim)_3COH$ and $(py)(mim)_2COH$ were recrystallized for microanalysis and n.m.r. spectroscopy, by dissolution in acetone–methanol, followed by exposure to diethyl ether vapour in a closed chamber.

Crystallography.—Crystals of the Et_3terpy complex were obtained from dichloromethane, and dissolution of the $(py)_2\text{-}CH_2$ complex in acetone resulted in formation of crystals on exposure to diethyl ether vapour in a closed chamber.

Unique data sets were measured to the specified $2\theta_{max.}$ limit at 295 K using a Syntex $P\bar{1}$ four-circle diffractometer fitted with a monochromatic Mo-K_α radiation source, and operating in conventional 2θ–θ scan mode. N Independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the basically 9 × 9 block-diagonal least-squares refinement after analytical absorption correction, and solution of the structure by the heavy-atom method. Anisotropic thermal parameters were refined for the non-hydrogen atoms; estimated values of (x,y,z) and $U_{iso.}$ for hydrogen atoms were included. Residuals R and R' (statistical weights) at convergence are quoted on $|F|$. Neutral complex scattering factors were used;[40] computation used the XTAL 83 program system implemented[41] by S. R. Hall on a Perkin-Elmer 3240 computer. Key results and atom numbering are given in Tables 2—8 and Figures 1 and 2.

Abnormal features. Peripheral ligand groups, *e.g.* ethyl groups, and nitrate and solvent molecules exhibited high thermal motion in some of the structures, resulting in unrealistic geometries. Residual difference map artefacts in (**10**) were modelled as (water molecule) oxygen fragments.

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References

1 M. Khan, R. C. Steevensz, D. G. Tuck, J. G. Noltes, and P. W. R. Corfield, *Inorg. Chem.*, 1980, **19**, 3407.
2 M. Veith and O. Recktenwald, *J. Organomet. Chem.*, 1984, **264**, 19.
3 M. A. Khan, C. Peppe, and D. G. Tuck, *J. Organomet. Chem.*, 1985, **280**, 17.
4 M. A. Khan, C. Peppe, and D. G. Tuck, *Organometallics*, 1986, **5**, 525.
5 F. Gerstner, W. Schwarz, H-D. Hausen, and J. Weidlein, *J. Organomet. Chem.*, 1979, **175**, 33.
6 C. Lecomte, J. Protas, P. Cocolios, and R. Guilard, *Acta Crystallogr., Sect. B*, 1980, **36**, 2769.
7 H. M. M. Shearer, J. Twiss, and K. Wade, *J. Organomet. Chem.*, 1980, **184**, 309.
8 A. M. Arif, D. C. Bradley, D. M. Frigo, M. B. Hursthouse, and B. Hussain, *J. Chem. Soc., Chem. Commun.*, 1985, 783.
9 T. L. Blundell and H. M. Powell, *Chem. Commun.*, 1967, 54.
10 K. Henrick, R. W. Matthews, B. L. Podejma, and P. A. Tasker, *J. Chem. Soc., Chem. Commun.*, 1982, 118; J. Crowder, K. Henrick, R. W. Matthews, and B. L. Podejma, *J. Chem. Res.*, 1983, (*S*) 82.
11 D. L. Hughes and M. R. Truter, *J. Chem. Soc., Chem. Commun.*, 1982, 727; *Acta Crystallogr., Sect. B*, 1983, **39**, 329.
12 A. J. Canty, K. Mills, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1986, 939.
13 K. Kobiro, S. Takada, Y. Odaira, and Y. Kawasaki, *J. Chem. Soc., Dalton Trans.*, 1986, 1767.
14 A. J. Canty, L. A. Titcombe, B. W. Skelton, and A. H. White, *Inorg. Chim. Acta*, 1986, **117**, L35.
15 A. J. Canty, N. Chaichit, B. M. Gatehouse, E. E. George, and G. Hayhurst, *Inorg. Chem.*, 1981, **20**, 2414.
16 S. S. Al-Juaid, N. H. Buttrus, C. Eaborn, P. B. Hitchcock, A. T. L. Roberts, J. D. Smith, and A. C. Sullivan, *J. Chem. Soc., Chem. Commun.*, 1986, 908.
17 D. G. Tuck, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, New York, 1982, vol. 1, pp. 684—723.
18 G. E. Coates and R. A. Whitcombe, *J. Chem. Soc.*, 1956, 3351.
19 G. Mann, H. Olapinski, R. Ott, and J. Weidlein, *Z. Anorg. Allg. Chem.*, 1974, **410**, 195.
20 H. Schmidbaur and F. Schindler, *Chem. Ber.*, 1966, **99**, 2178.
21 K. Mertz, W. Schwarz, B. Eberwein, J. Weidlein, H. Hess, and H. D. Hausen, *Z. Anorg. Allg. Chem.*, 1977, **429**, 99.
22 O. T. Beachley, C. Bueno, M. R. Churchill, R. B. Hallock, and R. G. Simmons, *Inorg. Chem.*, 1981, **20**, 2423.
23 M. R. P. van Vliet, P. Buysingh, G. van Koten, K. Vrieze, B. Kojic-Prodic, and A. L. Spek, *Organometallics*, 1985, **4**, 1701.
24 A. J. Canty, N. Chaichit, B. M. Gatehouse, and E. E. George, *Inorg. Chem.*, 1981, **20**, 4293.
25 D. L. White and J. W. Faller, *Inorg. Chem.*, 1982, **21**, 3119.
26 D. J. Szalda and F. R. Keene, *Inorg. Chem.*, 1986, **25**, 2795.
27 A. J. Canty, J. M. Patrick, and A. H. White, *Inorg. Chem.*, 1984, **23**, 3827.
28 P. K. Byers, A. J. Canty, B. W. Skelton, and A. H. White, *Aust. J. Chem.*, 1985, **38**, 1251.
29 P. K. Byers, A. J. Canty, N. J. Minchin, J. M. Patrick, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1985, 1183.
30 A. J. Canty, J. M. Patrick, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1983, 1873.
31 H. C. Clark and A. L. Pickard, *J. Organomet. Chem.*, 1967, **8**, 427.
32 L-C. Chao and R. D. Rieke, *J. Organomet. Chem.*, 1974, **67**, C64.
33 G. M. Badger and W. H. F. Sasse, *J. Chem. Soc.*, 1956, 616.
34 A. J. Canty and N. J. Minchin, *Aust. J. Chem.*, 1986, 39, 1063.
35 P. E. Rosevear and W. H. F. Sasse, *J. Heterocycl. Chem.*, 1971, **8**, 483.
36 C. C. Tang, D. Davalian, P. Huang, and R. Breslow, *J. Am. Chem. Soc.*, 1978, **100**, 3918.
37 A. J. Canty, E. E. George, and C. V. Lee, *Aust. J. Chem.*, 1983, **36**, 415.
38 J. P. Wibaut, A. P. De Jonge, H. G. P. van der Voort, and P. Ph. H. L. Otto, *Recl. Trav. Chim. Pays-Bas*, 1951, **70**, 1054.
39 R. S. Brown and J. Huguet, *Can. J. Chem.*, 1980, **58**, 889.
40 J. A. Ibers and W. C. Hamilton (eds.), 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
41 J. M. Stewart and S. R. Hall (eds.), 'The XTAL System,' Technical Report TR-1364, Computer Science Center, University of Maryland, 1983.

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