

Syntheses and crystal structures of three indium pyrazolyl complexes two of which contain novel bridging features

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The complexes $[(\text{HB}(\text{Pz}^*)_3)\text{In}(\mu\text{-Pz}^*)_2(\mu\text{-OH})\text{In}((\text{Pz}^*)_3\text{BH})]\text{I}\cdot 2\text{MeCN}$ **1**, $[\text{In}(\text{HB}(\text{Pz}^*)_3)\text{I}_2(\text{HPz}^*)]\cdot 0.5\text{C}_6\text{H}_{12}$ **2**, and $[\text{In}_2(\text{Pz}^{**})_4\text{I}_2\text{ONa}_2(\text{THF})_2]$ **3**, where HPz^* is 3,5-dimethylpyrazole and HPz^{**} is 3,5-di-*tert*-butylpyrazole, have been prepared and their crystal structures determined. The presence in **1** of bridging Pz^* and in **2** of monodentate HPz^* given that this was not a starting material is attributed to the moisture sensitivity of tris(pyrazolyl)borates. The indium ions in **1** are bridged by two Pz^* groups and an hydroxide ion, whereas in **3** the only bridge directly between the indium ions is an oxygen dianion. The four-co-ordinate donor set of the indium ion in **3** is formed by the bridging oxygen dianion, an iodide ion and the nitrogens of two Pz^{**} groups. The remaining nitrogens of the Pz^{**} co-ordinate to a sodium ion, which itself effectively bridges Pz^{**} groups on adjacent indium ions.

In an attempt to prepare and structurally characterise monomeric complexes of In^{I} we treated a variety of substituted tris(pyrazolyl)borates with InI . Tris(3-phenylpyrazolyl)- and tris(3-*tert*-butylpyrazolyl)-hydroboratoindium(I) complexes were formed and structurally characterised.^{1,2} However, with the less hindered tris(3,5-dimethylpyrazolyl)hydroborate InI gave the indium(III) complex $[\text{In}(\text{HB}(\text{Pz}^*)_3)_2]\text{I}$.³ Although not an indium(I) complex it was, nevertheless, of interest in that it represented the first example of a bicapped indium(III) species. Earlier attempts to synthesise such a complex using InCl_3 had produced $[\text{In}(\text{HB}(\text{Pz}^*)_3)\text{Cl}_2(\text{MeCN})]$.⁴ Although $[\text{In}(\text{HB}(\text{Pz}^*)_3)_2]\text{I}$ was structurally characterised the elemental and mass spectral analysis were at variance with the structure and it was an attempt to account for this discrepancy and also to synthesise the species directly that led to the work reported herein.

Experimental

All solvents were dried prior to use using standard procedures and reactions performed using Schlenk techniques under argon. Elemental analyses, C, H and N, on compounds **1** and **2** were carried out by Medac Ltd., and In, I, Na on **3** using a CAMSCAN CS44 scanning electron microscope. The ^1H NMR spectra were recorded in $[\text{D}_6]\text{dimethyl sulfoxide}$ on a Bruker AC 250 spectrometer using tetramethylsilane as an internal standard.

Syntheses

Compound 1. A small sample of $[\text{In}(\text{HB}(\text{Pz}^*)_3)_2]\text{I}$ **4** (0.5 g, 0.56 mmol) was boiled under reflux in 100 cm³ of wet acetonitrile (5% water) for two hours. The solution was filtered hot to give a white insoluble solid and a colourless filtrate which on standing overnight at -15°C gave colourless crystals of compound **1** as an acetonitrile solvate (0.6 g, yield 80%). Found: C, 43.54; H, 5.52; N, 21.00. Calculated for $\text{C}_{44}\text{H}_{65}\text{B}_2\text{IIn}_2\text{N}_{18}\text{O}$: C, 42.61; H, 5.28; N, 20.33%. We attribute these poor results to solvent dependence of the crystals.

Compound 2. To a solution of InI_3 (2.24 g, 4.52 mmol) in 50 cm³ of THF was added $\text{K}(\text{HB}(\text{Pz}^*)_3)$ (3.04 g, 8.04 mmol) and the reaction mixture stirred for 18 h. The solution was filtered to remove KI and the filtrate evaporated to dryness to produce an off white solid. This solid was recrystallised from 1:1

dichloromethane–hexane by slow evaporation. The pale yellow crystals produced were of X-ray quality (1.75 g, yield 50%). Found: C, 34.58; H, 4.40; N, 13.92. Calculated for $\text{C}_{23}\text{H}_{33}\text{BI}_2\text{InN}_8$: C, 34.96; H, 4.21; N, 14.71%.

Compound 3. To a solution of NaPz^{**} (HPz^{**} = 3,5-di-*tert*-butylpyrazole) (0.28 g, 4.14 mmol) in 50 cm³ of THF at -40°C was added with rapid stirring InI (1.00 g, 4.14 mmol). The suspension was left stirring until room temperature was reached. The resulting dark grey slurry was filtered through filter aid and the red filtrate evaporated to about 10 cm³ and left standing for several days at -15°C . The clear X-ray quality crystals that formed (*ca.* 0.014 g, yield < 0.5%) were analysed using a scanning electron microscope to give an approximate In:I:Na ratio of 1:1:1 consistent with the formulation $\text{In}_2(\text{Pz}^{**})_4\text{I}_2\text{ONa}_2(\text{THF})_2$.

Crystallography

Crystallographic details are given in Table 5. All data were recorded using a Delft-Instruments FAST TV area detector diffractometer following previously described procedures.⁵ Structures **1** and **3** were solved by direct methods and **2** by the heavy atom method. All refinement was by full matrix least squares. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms included in fixed positions.

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Results and discussion

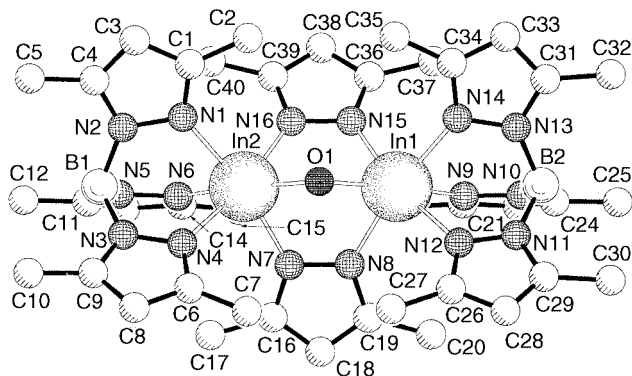
Although the compound $[\text{In}(\text{HB}(\text{Pz}^*)_3)_2]\text{I}$ **4** was characterised structurally, elemental and mass spectral analysis gave results which were at variance with the molecular structure.³ This observation together with the synthesis of **2** suggested to us that the ground samples used for elemental and mass spectral analysis of **4** had undergone partial hydrolysis on exposure to air/moisture. That this did not occur with the single crystal X-ray sample we attribute to the fact that it was stored under dry argon prior to data collection. The observed disparity led us to investigate this system in more detail and this was facilitated by boiling **4** under reflux in wet acetonitrile. The ^1H NMR of the X-ray quality crystals of **1** that formed gave signals in the δ 5.68 to 5.79 region, Table 1, which indicated that the pyrazolyl groups were not equivalent. This observation together with

Table 1 Proton NMR data for complexes **1** and **2** measured in $[\text{D}_6]\text{DMSO}$, reference SiMe_4

Complex	δ	Integration	Assignment
1	5.787	2	C13 and C23
	5.776	4	C3, C8, C28 and C33
	5.682	2	C18 and C38
	2.49	6	C12 and C25
	2.42	12	C17, C20, C37 and C40
	2.10	12	C5, C10, C30 and C32
	2.01	6	CH_3CN
	1.46	6	C15 and C22
	1.04	12	C2, C7, C27 and C35
	2	5.92	1
5.84		1	C3
5.77		2	C8 and C13
2.94		3	C2, C5, C7, C10, C12, C15, C17 and C20
2.44		3	
2.41		9	
2.09		6	
1.35		3	

Table 2 Selected bond lengths (\AA) and angles ($^\circ$) for complex **1**

In(1)–O(1)	2.134(6)	In(1)–O(1)–In(2)	111.8(3)
In(2)–O(1)	2.120(6)	O(1)–In(1)–N(9)	166.5(2)
In(1)–N(8)	2.238(8)	N(8)–In(1)–N(14)	170.6(2)
In(1)–N(15)	2.233(8)	N(12)–In(1)–N(15)	169.1(2)
In(2)–N(7)	2.230(7)	O(1)–In(2)–N(6)	167.5(2)
In(2)–N(16)	2.244(7)	N(1)–In(2)–N(7)	169.5(2)
In(1)–N(9)	2.248(7)	N(4)–In(2)–N(16)	170.1(2)
In(1)–N(12)	2.288(8)	O(1)–In(1)–N(8)	80.8(3)
In(1)–N(14)	2.263(8)	O(1)–In(1)–N(14)	105.6(3)
In(2)–N(1)	2.277(8)	O(1)–In(1)–N(15)	83.2(3)
In(2)–N(4)	2.280(8)	O(1)–In(2)–N(7)	82.1(3)
In(2)–N(6)	2.248(7)	O(1)–In(2)–N(1)	106.1(3)
		O(1)–In(2)–N(16)	83.0(3)

**Fig. 1** The molecular structure of compound **1** from which H, I^- and solvent molecules have been omitted.

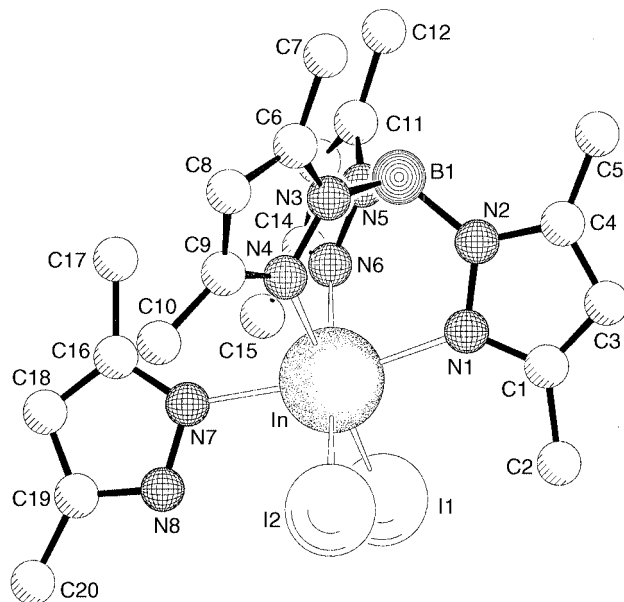
the elemental analysis led us to carry out an X-ray structural determination.

Fig. 1 shows the structure of compound **1** from which the hydrogen atoms, iodide ion and solvent molecules have been omitted. Table 2 lists selected bond lengths and angles. As can be seen from Fig. 1 each In^{III} is six-co-ordinate with a N_2O donor set, the O being shared between the two octahedra. That the bridging O is protonated was deduced from charge considerations.

The average In–N (of $\text{HB}(\text{Pz}^*)_3^-$) bond length at 2.267(8) \AA is similar to that in compound **4** (2.249(5) \AA).³ The In–N bond length in the pyrazolide bridge is not significantly different at 2.236(8) \AA and is similar to that in $\text{In}(\text{CH}_3)_2(\text{N}_2\text{C}_3\text{H}_3)$, average 2.209(5) \AA ,⁶ and $[\text{In}_2\text{Cl}_4(\text{C}_8\text{H}_6\text{N}_2)(\text{DMF})_2] \cdot 2\text{DMF}$, average 2.208 \AA .⁷ Comparing the In–O bond length in **1**, 2.127(6) \AA , to that in $[\text{In}_2(\text{AcO})_4(\mu\text{-O})(\text{tacn})_2]$ ($\text{tacn} = 1,4,7\text{-triazacyclononane}$) 2.115(4) \AA ,⁸ and $[\text{O}\{\text{(Me}_2\text{Si)}_3\text{CIn}\}_4(\text{OH})_6]$, 2.17(2) ($\mu\text{-OH}$)

Table 3 Selected bond lengths (\AA) and angles ($^\circ$) for complex **2**

In(1)–I(1)	2.837(4)	In(1)–N(4)	2.291(7)
In(1)–I(2)	2.839(4)	In(1)–N(6)	2.274(7)
In(1)–N(1)	2.262(7)	In(1)–N(7)	2.311(7)
I(1)–In(1)–I(2)	93.2(1)	I(1)–In(1)–N(6)	93.5(2)
I(1)–In(1)–N(1)	96.3(2)	I(2)–In(1)–N(6)	173.3(1)
I(2)–In(1)–N(1)	95.0(2)	N(1)–In(1)–N(4)	85.5(3)
I(1)–In(1)–N(7)	89.9(2)	N(1)–In(1)–N(6)	83.5(3)
I(2)–In(1)–N(7)	92.4(2)	N(1)–In(1)–N(7)	170.0(2)
I(1)–In(1)–N(4)	175.3(1)	N(4)–In(1)–N(7)	87.7(3)
I(2)–In(1)–N(4)	90.9(2)	N(6)–In(1)–N(7)	88.3(3)

**Fig. 2** The molecular structure of compound **2** from which hydrogen atoms have been omitted.

and 2.12(2) \AA ($\mu_4\text{-O}$),⁹ shows them to be very similar, whereas the In–O–In angles vary from 111.8(3) ($\mu\text{-OH}$), 142.5(2) ($\mu\text{-O}$)⁸ and 109.5(8) ($\mu_4\text{-O}$) and 105.5(5) ($\mu\text{-OH}$)⁹ respectively. The $\text{In} \cdots \text{In}$ distance in **1**, 3.497(4) \AA , precludes any interaction.¹⁰

To see if it was possible to form $[\text{In}(\text{HB}(\text{Pz}^*)_3)_2]^+$ directly from In^{III} and reasoning that the lower lattice energy of InI_3 compared to InCl_3 might facilitate this, $\text{K}(\text{HB}(\text{Pz}^*)_3)$ was treated with InI_3 . Instead of the expected bicapped species $[\text{In}(\text{HB}(\text{Pz}^*)_3)_2]\text{I}$ the complex $[\text{In}(\text{HB}(\text{Pz}^*)_3)_2\text{I}_2(\text{HPz}^*)] \cdot 0.5\text{C}_6\text{H}_{12}$ **2** formed. Fig. 2 shows the structure of **2** and Table 3 lists selected bond lengths and angles. The six-co-ordination is achieved with a N_4I_2 donor set resulting in a slightly distorted octahedron. The average In–N (of $\text{HB}(\text{Pz}^*)_3^-$) bond length, 2.276(7) \AA , is similar to that in **1** with the remaining bond lengths and angles being unexceptional. The presence in **2** of HPz^* is interesting though not entirely unexpected given the moisture sensitivity of tris(pyrazolyl)borates.¹¹

Since the breakdown products Pz^* and HPz^* of $\text{HB}(\text{Pz}^*)_3^-$ occur in complexes **1** and **2** respectively it seemed to us that direct reaction of a sodium pyrazolide with an indium iodide would be worth investigating. We therefore treated NaPz^* and NaPz^{**} with InI_3 and InI in THF. It was only with InI and NaPz^{**} that a tractable product, albeit in very low yield, was obtained, **3**. The In:I:Na ratio of the air sensitive crystals of **3** was sufficiently perplexing to justify an X-ray crystallographic structure determination. Fig. 3(a) and 3(b) show the molecular structure of **3** and Table 4 lists selected bond lengths and angles. The structure shows two indium(III) ions bridged by an O^{2-} with an In–O distance of 1.990(6) \AA . This is shorter than the corresponding distance in **1** (2.127(6) \AA) and $[\text{In}_2(\text{AcO})_4(\mu\text{-O})(\text{tacn})_2]$ (2.115(4) \AA).⁸ At 138.0(9) $^\circ$ the bridge angle in **3** is

much larger than that in **1** (111.8(3)°) but similar to that in $[\text{In}_2(\text{AcO})_4(\mu\text{-O})(\text{tacz})_2]$ (142.5(2)°).⁸ The In–N distances in **3** (2.073(17) and 2.118(18) Å) are significantly shorter than the corresponding distance in **2** (2.311(7) Å). The non-bonded In...N distances in **3** are 2.68 and 2.91 Å and both are less than the non-bonded In...N distance in **2** (3.15 Å) the shorter distance being substantially so. Four-co-ordination about each In is completed by an iodide ion at 2.673(2) Å, somewhat shorter than the In–I distance in **2** (2.838(4) Å). The angles about the In define a distorted tetrahedron.

The geometry of the sodium ion is best described as a grossly flattened tetrahedron with Na–O distances of 2.313(13) Å (to $\mu\text{-O}$) and 2.262(19) Å (to THF) and Na–N distances of 2.430(19) and 2.418(19) Å. In the complex $[\{\text{Ni}(\text{salophen})\text{Na}(\text{THF})_3\}_2] \cdot \text{C}_4\text{H}_8\text{O}_2$ [$\text{H}_2\text{salophen} = N,N'$ -bis(salicylidene)-*o*-phenylenediamine] the Na–O bond lengths are (to salophen) 2.281 and 2.284 and (to THF) 2.423, 2.345 and 2.329 Å.¹² Fig. 3(b) shows the position of the hydrogen atoms on C(512) with respect to Na(1). One of these hydrogens is at 2.34 Å from Na(1), a distance short enough to suggest a Na...H interaction.¹³

Given the syntheses and structures of compounds **1**, **2**, and **3** there is clearly a need for further work on this system to verify the validity or otherwise of the various reaction schemes that naturally suggest themselves, e.g. equations (1)–(3). In view of

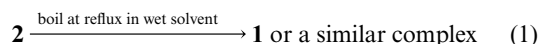


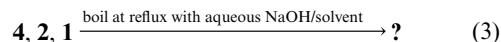
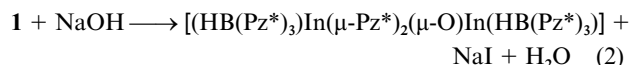
Table 4 Selected bond lengths (Å) and angles (°) for complex **3**

In(1)–O(1)	1.990(6)	In(1)–O(1)–In(1')	138.0(9)
In(1)–N(21)	2.118(18)	Na(1)–O(1)–Na(1')	97.6(7)
In(1)–N(22)	2.073(17)	O(1)–Na(1)–O(2)	116.9(7)
In(1)–I	2.673(2)	N(11)–Na(1)–N(12')	165.1(7)
Na(1)–O(1)	2.313(13)	O(2)–Na(1)–N(12')	88.1(7)
Na(1)–O(2)	2.262(19)	O(1)–Na(1)–N(12')	87.2(5)
Na(1)–N(11)	2.418(19)	O(2)–Na(1)–N(11)	91.2(7)
Na(1)–N(12')	2.430(19)	O(1)–Na(1)–N(11)	79.8(5)
In...N(12)	2.68 non-bonded	O(1)–In(1)–N(21)	100.1(7)
In...N(11)	2.91 non-bonded	O(1)–In(1)–N(22)	99.5(4)
		O(1)–In(1)–I	113.8(3)
		N(22)–In(1)–I	122.2(4)
Na(1)–H(51B)	2.34	N(21)–In(1)–I	112.5(5)
		N(21)–In(1)–N(22)	106.0(7)

Symmetry transformation used to generate equivalent atoms: ' – x , – y + 1, z .

Table 5 Crystallographic data for complexes **1**–**3**

	1	2	3
Formula	$\text{C}_{44}\text{H}_{65}\text{B}_2\text{In}_2\text{N}_{18}\text{O}$	$\text{C}_{23}\text{H}_{33}\text{BI}_2\text{InN}_8$	$\text{C}_{52}\text{H}_{92}\text{I}_2\text{In}_2\text{N}_8\text{Na}_2\text{O}_3$
M	1240.29	790.20	1406.96
Crystal system	Orthorhombic	Monoclinic	Tetragonal
Space group	$Pna2_1$	$P2_1$	$P\bar{4}$
$a/\text{Å}$	13.752(7)	11.468(2)	16.664(3)
$b/\text{Å}$	17.045(1)	16.341(9)	16.664(3)
$c/\text{Å}$	23.055(16)	16.783(1)	11.948(8)
$\beta/^\circ$		101.50(1)	
$V/\text{Å}^3$	5404.79	3081.97	3318.2
Z	4	4	2
$D_c/\text{Mg m}^{-3}$	1.525	1.703	1.408
μ/mm^{-1}	1.42	2.75	1.58
$F(000)$	2496	1528	1420
Reflections measured	25028	15139	14686
Reflections unique	13124	6684	5321
Reflections observed	8060	4954	1977
Significance test	$F_o > 4\sigma(F_o)$	$F_o > 3\sigma(F_o)$	$F_o > 4\sigma(F_o)$
$R1$	0.044 (for 8060 data)	0.038 (for 4954 data)	0.059 (for 1977 data)
Number of parameters	653	352	331
Maximum, minimum electron density/ $e \text{ Å}^{-3}$	2.35, –1.21	0.95, –0.87	1.05, –0.78



our synthesis of $[\text{Ga}_4(\text{OH})_6(3\text{-}^t\text{BuPzH})_{10}\text{I}_6] \cdot 2\text{MeCN}$, a quasi double heterocubane, by the reaction of GaI_3 with $\text{K}[\text{HB}(3\text{-}$

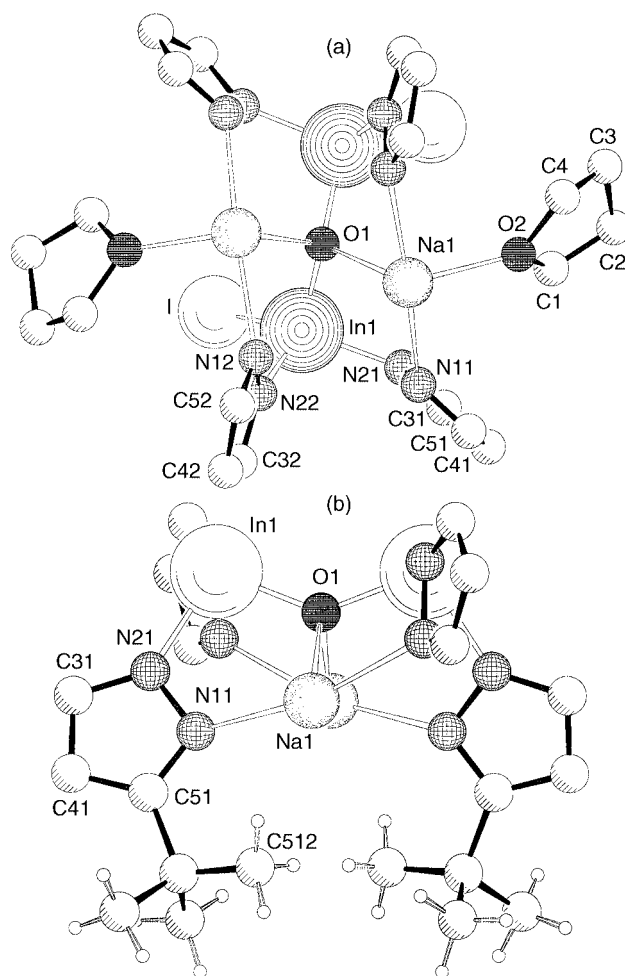


Fig. 3 The molecular structure of compound **3** from which (a) the tertiary butyl groups have been omitted and (b) six of these groups have been omitted.

'BuPz)₃] in THF,¹⁴ this last set of reactions (3) would be of particular interest to see if it could lead to In/O complexes of higher nuclearity.

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