Synthesis and structural characterisation of a soluble, metastable indium(I) halide complex, [InBr(tmeda)]†

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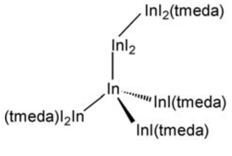
The first example of an indium(I) halide complex, [InBr(tmeda)], has been prepared by the reversible dissolution of InBr in a tmeda–toluene mixture. The structural characterisation of the metastable compound shows it to be monomeric with weak In···In interactions in the solid state. In solution, it decomposes to either InBr or $[In_2Br_4(tmeda)_2]$.

The commercial availability of the indium(I) halides, InX (X = Cl, Br or I), has allowed the low oxidation state chemistry of the metal to flourish over the past two decades.[1] For example, these salts have been used as precursors in the preparation of molecular indium(I) organometallics,[2] mixed valence indium species,[3] heterometallic clusters[4] and inorganic materials containing In^+ cations.[1] In addition, indium(I) halides are finding increasing use in stoichiometric and catalytic organic transformations.[5] Despite their importance, there are problems associated with these reagents. The most limiting of these is their vanishingly low solubility in non-coordinating solvents. As a result, many of their reactions require coordinating solvents to be effective to any degree. However, given that indium(I) halides can rapidly disproportionate to indium(II) and indium(III) halides in coordinating solvents,[1] the outcomes of these reactions are not always straightforward or predictable. Remarkably, almost nothing is known about the mechanism by which indium(I) halides dissolve in coordinating solvents, and whether or not this involves soluble indium(I) species at all.[6] Indeed, there are no known examples of structurally characterised molecular indium(I) halide complexes.[7,8] This is perhaps surprising when it is considered that a range of soluble, metastable aluminium(I) and gallium(I) halide complexes, $[M_mX_m(L)_n]$ (M = Al or Ga; L = ether, amine or phosphine), have been prepared and their remarkable further chemistry well developed.[9] The structural characterisation of several examples of these complexes ($[Al_4I_4(PEt_3)_4]$,[10] $[Al_4Br_4(NEt_3)_4]$[11] and $[Ga_8I_8(PEt_3)_6]$[12]) show all to possess aluminium or gallium centres covalently bonded to one halide and two other metals. As a result, although formally in the +1 oxidation state, their metal centres should be considered as trivalent.[13] To some extent, this must explain the metastability of the complexes, $[M_mX_m(L)_n]$.

We have begun to examine the mechanism by which solid indium(I) halides interact with donor solvents and other Lewis bases. This study was inspired by a number of early reports which indicated that InX can form soluble adducts with N-donor ligands without undergoing disproportionation.[1] Of most relevance here, is the work of Tuck *et al.* who found InX (X = Br or I) to dissolve in toluene–tmeda (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) mixtures to yield solutions having concentrations of up to 15.7×10^{-3} M.[14] From these, solids analysing as $InX(tmeda)_{0.5}$ were precipitated by the addition of hexane. In the case of indium(I) iodide, we have recently shown that the precipitated solid is, in fact, the novel indium sub-halide cluster complex, $[In_6I_8(tmeda)_4]$ **1** (average In oxidation state: +1.33).[15] We have also demonstrated that the reaction of InBr with toluene–quinuclidine mixtures gives the related anionic indium cluster complex, **2**.[15,16] As an extension of that work, we now report the synthesis and structural characterisation of the first molecular indium(I) halide complex, [InBr(tmeda)], and briefly discuss the bearing this result will have on synthetic chemists.



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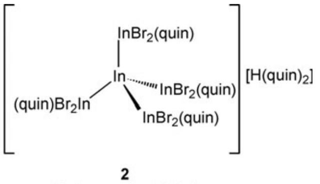

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(quin = quinuclidine)

Using a modification of the method of Tuck *et al.*,[14] InBr powder was suspended in a 10% v/v tmeda–toluene mixture at −85 °C (Scheme 1). Upon warming, dissolution of the InBr commenced at −60 °C and was complete by −30 °C, yielding an yellow-orange solution. Concentration of the solution at this temperature led to the deposition of a blue-violet microcrystalline solid which, upon isolation, decomposed at 20 °C over several hours to a grey solid. Similarly, warming the yellow-orange solution above −20 °C led to indium metal deposition and the eventual isolation of the known indium(II) complex, $[In_2Br_4(tmeda)_2]$ (see ESI† for details of its X-ray crystal structure).[14,17] In order to obtain X-ray quality crystals of the blue-violet solid, the yellow-orange solution was filtered and the filtrate carefully layered with hexane at −80 °C in a long, thin Schlenk flask (*ca.* 40 cm by 1 cm). After approximately two weeks at this temperature, yellow crystals had grown at the solution/hexane interface and red-purple crystals had grown *ca.* 2 cm above it. The crystals were isolated and, surprisingly, upon warming above −30 °C, the yellow crystals rapidly and irreversibly changed colour to blue-violet with retention of their crystallinity. This material was structurally

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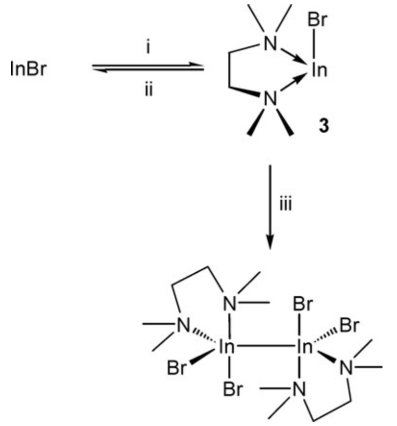
† Electronic supplementary information (ESI) available: Full synthetic and spectroscopic details; ORTEP diagrams for $[In_2Br_4(tmeda)_2]$ and $[(quin)_2H][In_5Cl_8(quin)_5]$; full details and references for the theoretical studies. CCDC 699631–699633. For ESI and crystallographic data in CIF or other electronic format, see DOI: 10.1039/b814658f



Scheme 1 Reagents and conditions: i, tmeda–toluene; ii, −tmeda; iii, > −20 °C, −In(s).

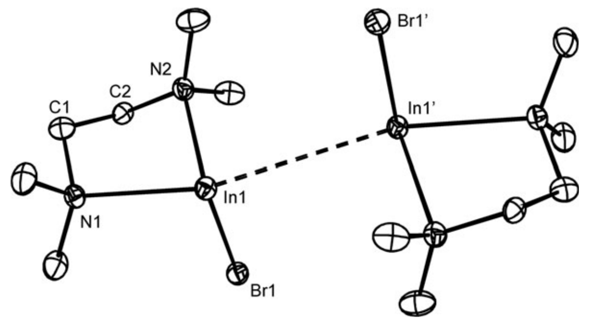


Fig. 1 Molecular structure of **3** (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): In(1)···In(1)′ 3.678(2), In(1)–N(2) 2.500(5), In(1)–N(1) 2.531(4), In(1)–Br(1) 2.7579(8), N(2)–In(1)–N(1) 72.98(14), N(2)–In(1)–Br(1) 92.21(12), N(1)–In(1)–Br(1) 88.44(11). Symmetry operation: −*x*, 1 − *y*, −*z*.

characterised as [InBr(tmeda)] **3** (*vide infra*), while the red-purple crystals were found to be a known structural modification of InBr.[18] Compound **3** could also be obtained in a 28% yield by placing the aforementioned yellow-orange solution at −80 °C for 7 days.

These experiments confirm Tuck's assertion that InBr dissolves in tmeda–toluene mixtures without disproportionation below −20 °C, and that disproportionation to $[\mathrm{In_2Br_4(tmeda)_2}]$ occurs above −20 °C. Moreover, the presence of single crystals of InBr above those of **3** in the crystallisation Schlenk flask, indicates that solutions of **3** are in equilibrium with tmeda and solid InBr. In this equilibrium, the deposition of InBr is favoured as the tmeda concentration diminishes by diffusion of hexane into the tmeda–toluene solution of **3**. We believe that such a crystallisation of an indium(I) halide from an organic solvent is unprecedented. Based on our results, it seems likely that the solid material Tuck obtained from his experiments, *viz*. $\mathrm{InBr(tmeda)_{0.5}}$, was a mixture of two or more of the following: **3**, InBr, $[\mathrm{In_2Br_4(tmeda)_2}]$ or $\mathrm{In_{(s)}}$.

Considering the different outcomes from the reactions of InI and InBr with tmeda in toluene, we examined the related reaction with InCl. This led to the dissolution of the salt and the formation of a red-orange solution which was found to be much more sensitive to disproportionation processes than solutions of the other two materials. Efforts to obtain crystalline solids from this solution were not successful. It is noteworthy, however, that the reaction of quinuclidine with InCl in toluene led to a good yield of a mixed oxidation state cluster complex closely related to **2**, *viz*. $[\mathrm{(quin)_2H}][\mathrm{In_5Cl_8(quin)_5}]$, but with one of its $\mathrm{InCl_2}$ fragments coordinated by two quinuclidine ligands (see ESI† for details of its X-ray crystal structure). These differences between **2** and $[\mathrm{(quin)_2H}][\mathrm{In_5Cl_8(quin)_5}]$ likely arise from the lesser steric strain placed upon the anion by the smaller size of the halide ligands in the latter, relative to those in former.

Compound **3** is not soluble in normal deuterated solvents without the addition of tmeda. As a result, meaningful NMR spectroscopic data for the compound could not be obtained and, therefore, its characterisation relied on a crystallographic analysis.‡ The molecular structure of the compound is displayed in Fig. 1, which shows it to consist of monomeric units having long range In···In interactions (3.678(2) Å). These are well outside the sum of two In covalent radii (2.84 Å[19]) but just inside double the sum of the van der Waals radius for the metal (3.86 Å[20]). Accordingly, they should be considered as no more than weak, non-directional interactions.[21] This situation differs to that in all structurally characterised aluminium(I) and gallium(I) halide complexes which possess metal–metal covalent bonds. It also highlights an analogy between **3** and monomeric group 13 metal(I) diyls, :MR (R = bulky alkyl, aryl *etc*.), which have a substantial coordination chemistry derived from their Lewis basic metal lone pairs.[2] The geometry of the indium centre in **3** is distorted pyramidal with acute angles about the metal (Σ angles = 253.6°) that are suggestive of a high degree of s-character to its lone pair. Although the In centre is only 3-coordinate, both its N–In distances and the In–Br distance are at the upper end of the known ranges.[22] This is not surprising, considering that the metal is in the monovalent state and would be expected to have a larger radius than in higher oxidation state systems. It is also of no surprise that the In–Br distance is shorter than the closest contact in the crystal structure of InBr (3.01 Å - closest of 7 contacts in the range 3.00–3.90 Å[18]), but significantly longer than that for monomeric InBr in the gas phase (2.543 Å[1]).

We were intrigued by the colour change (from yellow to blue-violet) that crystals of **3** underwent at −30 °C. A number of attempts were made to obtain the crystal structure of the yellow form of the compound, but all were thwarted by the temperature sensitivity of this modification. It seems likely, however, that the colour change is associated with an irreversible, non-destructive phase change of the crystals.

In order to probe the electronic structure of **3**, *ab initio* calculations were carried out on it at the MP2 level of theory. The geometry of the optimised gas phase structure, which was found to be a minimum by analysis of vibrational modes, is in excellent agreement with that from the X-ray crystal structure. The In–Br (2.796 Å) and In–N bond lengths (2.6055 Å, mean) are overestimated by *ca.* 1% and 4%, respectively, whilst the Br–In–N angles (86.7° and 90.0°) are underestimated by less than 3%. An NBO analysis indicated that the indium lone pair is predominantly associated with the HOMO (Fig. 2) and has high s-character (93.2% s-, 6.76% p-character), while the In–Br bond exhibits appreciable ionic character

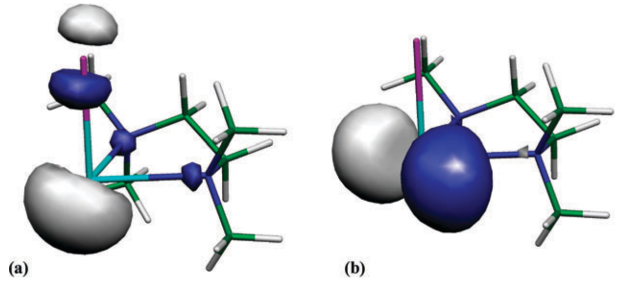


Fig. 2 Representations of (a) the HOMO and (b) the LUMO of [InBr(tmeda)].

(natural charges: In +0.74, Br −0.81; Wiberg bond index: 0.33). The LUMO (Fig. 2) corresponds principally to a vacant p-orbital at the In centre.

In conclusion, InBr has been shown to dissolve in tmeda–toluene mixtures to give solutions that are stable with respect to disproportionation up to −20 °C. Crystallisation of the first indium(I) halide complex, [InBr(tmeda)], from these solutions has been achieved, and the compound shown to be monomeric by X-ray crystallography. This result differs significantly from the dissolution of InI in tmeda–toluene mixtures, which yields the cluster complex [In_6I_8(tmeda)$_4$]. The propensity of indium(I) halides to disproportionate in most coordinating solvents is a shortcoming of these important reagents that has, no doubt, led to many reactions involving them being unsuccessful in the past. We suggest that synthetic chemists requiring well defined, soluble indium(I) halide reagents consider using solutions of InBr in 10% tmeda–toluene at temperatures below −20 °C.[23] In our laboratory we are currently examining the synthetic utility of such solutions, in addition to the use of **3** as an In-donor ligand towards transition metal fragments (*cf.* group 13 metal(I) alkyls).[24] We will report on these endeavours in due course.

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‡ *Crystal data* for **3**: $C_6H_{16}BrInN_2$, M = 310.94, monoclinic, space group $P2_1/c$, a = 7.3609(15) Å, b = 14.693(3) Å, c = 10.264(2) Å, β = 104.82(3)°, V = 1073.2(4) Å^3, Z = 4, D_c = 1.925 g cm^{-3}, F(000) = 600, μ(Mo-Kα) = 5.870 mm^{-1}, 123(2) K, 1869 unique reflections [R(int) 0.0293], R (on F) 0.0360, wR (on F^2) 0.0902 ($I > 2\sigma I$); **[In_2Br_4(tmeda)$_4$]**: $C_{12}H_{32}Br_4In_2N_4$, M = 781.70, orthorhombic, space group $Pbca$, a = 17.327(4) Å, b = 12.110(2) Å, c = 22.420(5) Å, V = 4704.4(16) Å^3, Z = 8, D_c = 2.207 g cm^{-3}, F(000) = 2960, μ(Mo-Kα) = 8.757 mm^{-1}, 123(2) K, 4317 unique reflections [R(int) 0.1382], R (on F) 0.0552, wR (on F^2) 0.1493 ($I > 2\sigma I$). **[(quin)$_2$H][In_5Cl_8(quin)$_5$]**: $C_{49}H_{92}Cl_8In_5N_7$, M = 1637.00, triclinic, space group $P\bar{1}$, a = 12.079(2) Å, b = 21.690(4) Å, c = 12.363(3) Å, α = 90.38(3)°, β = 97.84(3)°, γ = 103.65(3)°, V = 3115.5(11) Å^3, Z = 2, D_c = 1.745 g cm^{-3}, F(000) = 1632, μ(Mo-Kα) = 2.204 mm^{-1}, 150(2) K, 10 832 unique reflections [R(int) 0.0477], R (on F) 0.1097, wR (on F^2) 0.3065 ($I > 2\sigma I$). For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b814658f

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