Cluster Compounds

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“Dissolution” of Indium(I) Iodide: Synthesis and Structural Characterization of the Neutral Indium Sub-Halide Cluster Complex $[In_6I_8(tmeda)_4]$**

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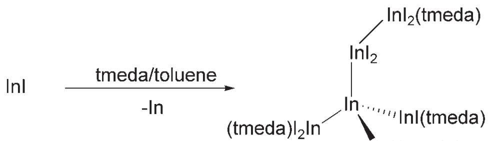
The chemistry of low oxidation state indium compounds has been extensively investigated over the past 20 years.[1] Undoubtedly, the most important compounds in this field are the indium(I) halides InX (X = Cl, Br, or I), all of which are commercially available and have found numerous applications as, for example, reagents for organic[2,3] and organometallic[1] synthetic methodologies; the preparation of multicomponent inorganic materials containing In^+ cations;[1] and the construction of heterometallic clusters.[1,4] Despite this, these compounds have drawbacks in their use as reagents for organic transformations and in the preparation of molecular compounds. These include their extremely low solubility in noncoordinating organic solvents and their propensity to rapidly disproportionate to In^{II} or In^{III} halide complexes when treated with coordinating solvents.[1] Given that many reactions involving indium(I) halides require coordinating solvents to proceed,[1–4] it is very surprising that almost nothing is known of the nature of the intermediates in these disproportionation processes,[5] and accordingly there are no structurally characterized examples of indium(I) halide complexes. In contrast, a variety of soluble, “metastable” oligomeric aluminum(I) and gallium(I) halide complexes $[\{MX(L)\}_n]$ (M = Al or Ga, X = halide, L = ether, amine, or phosphine) are known, and several have been structurally authenticated. In addition, the mechanisms involved in the disproportionation of these complexes are becoming understood, and control over these processes has led to an array of novel metal halide cluster complexes ($[M_xX_y(L)_z]$) with average metal oxidation states of less than +1 ($x > y$) or greater than +1 ($x < y$).[6] There are no related complexes for indium,[7] and the only known mixed oxidation state sub-halide complex for this metal ($[(quin)_2H][In_5Br_8(quin)_4]$; quin = quinuclidine) is anionic. This complex is formed by the thermal decomposition of an indium trihydride complex ($[InH_3(quin)]$, in the presence of LiBr) via the isolated intermediate $[InH_2Br(quin)]$.[8]

In view of the importance of indium(I) halides to the synthetic chemist, it would be of great interest to access well defined, soluble examples of their complexes with Lewis bases (c.f. Al^I and Ga^I halides), the reactivity of which should be more controllable than insoluble InX. It would be of equal interest to explore the controlled disproportionation of such compounds, which could potentially lead to as yet unknown neutral indium sub-halide cluster complexes. Several soluble indium(I) salts (e.g. InO_2SCF_3[9] and $InBF_4$[10]) have been structurally characterized and proposed as synthetic alternatives to indium(I) halides, although this possibility is yet to be realized to any great extent. Although no indium(I) halide complexes have been fully characterized, a number of early reports have suggested that InX can form partially soluble adducts with amine donors.[1] In perhaps the most pertinent of these reports, Tuck and co-workers describe the dissolution of InX (X = Br or I) in toluene/tmeda mixtures (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) to yield solutions with concentrations of up to 15.7×10^{-3} M from which solids with the assigned empirical formula $[InX(tmeda)_{0.5}]$ can be precipitated by the addition of hexane.[11] As part of an ongoing study of indium sub-halide complexes, we were intrigued to ascertain the structural composition of these solids, which in the case of X = I is shown herein to be $[In_6I_8(tmeda)_4]$, the first neutral indium sub-halide cluster complex.

The addition of a 12 % v/v tmeda/toluene mixture to InI at −80 °C led to its dissolution above −50 °C and the formation of a red-orange solution. Warming to 20 °C led to no further color change. Filtration of the solution and subsequent cooling to −30 °C (or layering with excess hexane at 20 °C) afforded a high yield (75 % based on iodide) of the cluster complex $[In_6I_8(tmeda)_4]$ (**1**, Scheme 1). Similar yields of **1** were obtained when more concentrated tmeda/toluene mixtures were employed, or if the red-orange solution was not allowed to warm past −20 °C before or during workup. The



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Scheme 1. The preparation of $[In_6I_8(tmeda)_4]$ (**1**).

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latter reaction conditions were those used in Tuck's original study,[11] which suggests that his precipitated material ([InI(tmeda)$_{0.5}$]) was probably **1**. This seems reasonable as the original analysis of [InI(tmeda)$_{0.5}$] was poor. When InBr was treated with tmeda/toluene mixtures under the conditions used for InI, significant amounts of a blue-purple microcrystalline material were obtained. Tuck obtained a similar material in his study which analyzed well for [InBr(tmeda)$_{0.5}$]. Interestingly, our analysis of this compound suggests its formula is [InBr(tmeda)], which is not only different to that of the previous report but indicates that it does not have the same structural motif as **1**. Although we have not yet been able to obtain its solid-state structure, efforts continue towards this goal.

The mechanism of formation of **1** presumably involves partial disproportionation of InI upon treatment with tmeda. Consistent with this proposal is the deposition of the expected amount of indium metal during the reaction. The fact that the disproportionation process does not proceed at ambient temperature past a complex with an average indium oxidation state of $+1.33$ is unprecedented, as all previously reported reactions of indium halides with Lewis bases have yielded compounds with average metal oxidation states of $+2$ or $+3$.[1] Although compound **1** is stable at ambient temperature it will decompose in the solid state or in solution at temperatures in excess of 60 °C to give high yields of the known indium(II) complex [(tmeda)I_2InInI_2(tmeda)],[12] which has been crystallographically characterized for the first time (see the Supporting Information for details). The formation and stability of **1** prompted us to reinvestigate the mechanism of formation of the aforementioned salt [(quin)$_2$H][In$_5$Br$_8$(quin)$_4$].[8] We have found that this complex is formed in moderate yield (ca. 40 %) in the reaction of InBr with an excess of quincuclidine in toluene. This result provides good evidence for our original proposal that the salt arises from reductive elimination of H_2 from [InH$_2$Br(quin)], thus generating "In^{I}Br(quin)", which subsequently undergoes a series of disproportionation and other reactions. It also proves our original contention that the proton of the quinuclidinium cation was not derived from the indium hydride fragment, but probably originates from the solvent.

Although **1** is diamagnetic, its ^{1}H and ^{13}C{^{1}H} NMR spectra are not very informative and display only broad signals corresponding to the tmeda ligands. The broadness of these signals is probably due to the speed of rotation of the terminal {InI$_n$(tmeda)} fragments ($n = 1$ or 2) about the In–In bonds of the complex being approximately equivalent to the NMR timescale. Variable-temperature ^{1}H and ^{13}C{^{1}H} NMR studies were carried out on solutions of the complex in [D$_8$]toluene, but its low solubility in this solvent below −20 °C did not permit any resolution of these spectra to be observed. No signals were observed in the ^{115}In{^{1}H} NMR spectrum of the complex, presumably because of the quadrupolar nature of that isotope ($I = 9/2$). The UV/Vis spectrum of the complex displays a moderately strong absorption in the visible region ($\lambda_{max} = 381.0$ nm, $\varepsilon_{max} = 10410\ \text{M}^{-1}\text{cm}^{-1}$), the origin of which has been investigated by a DFT study (see below). It is of note that **1** can be repeatedly dissolved in, and recrystallized from, toluene at 20 °C without detectable decomposition. This fact combined with its limiting solubility in this solvent (3.4×10^{-3} M at 293 K) or 10 % v/v tmeda/toluene (8.6×10^{-3} M at 293 K) could allow the compound to be used, for example, as a soluble source of "InI" for controlled organic transformations or salt metathesis reactions. Indeed, it is likely that when such reactions have been carried out in the past with InI in donor solvents, soluble mixed oxidation state indium iodide complexes (such as **1**) are the transient reactive species.

The X-ray crystal structure of **1** is depicted in Figure 1 and shows it to be monomeric with a central branched In$_6$ chain with the indium centers having formal oxidation states of $+2$ (In3, In5, and In6; each possessing two iodide ligands), $+1$ (In1 and In2; each possessing one iodide ligand), or 0 (In4; bonded only to In centers). All In–In bond lengths are in the normal range,[13] although the In1–In4 bond is significantly longer than the others (compare with a mean In–In bond length of 2.747 Å in [(quin)$_2$H][In$_5$Br$_8$(quin)$_4$]). Similarly, the In–I bond lengths lie in the known range,[13] although In3–I3 and In6–I8 are more than 0.3 Å longer than the other In–I bond lengths in the compound as these iodine centers occupy axial sites of the distorted trigonal bipyramidal coordination geometries of In3 and In6 (the other In centers have distorted tetrahedral geometries). The four tmeda ligands in the complex chelate the terminal indium centers In1, In2, In3, and In6 with normal In–N bond lengths. Notably, the discrete molecular structure of **1** differs from the solid-state structures

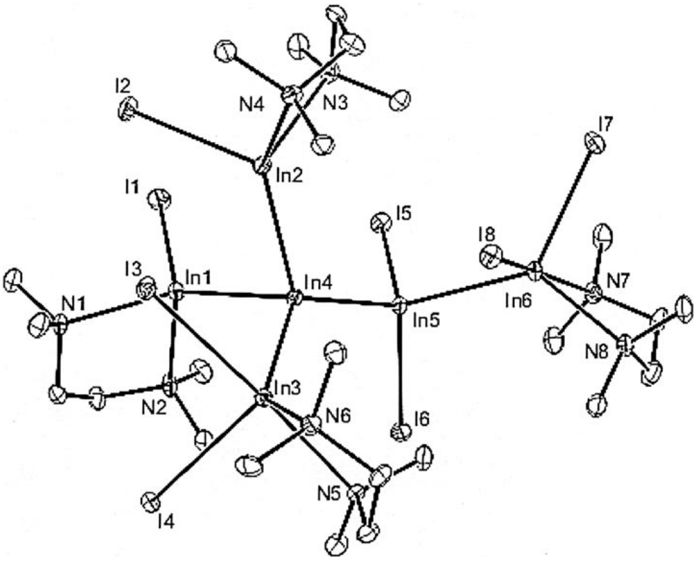

Figure 1. Structure of **1** (25 % ellipsoids; H atoms omitted for clarity). Relevant bond lengths [Å] and angles [°]: I1–In1 2.7833(10), I2–In2 2.8010(10), I3–In3 3.1363(9), I4–In3 2.8119(9), I5–In5 2.8425(10), I6–In5 2.8445(9), I7–In6 2.7697(10), I8–In6 3.2392(10), In1–N1 2.355(6), In1–N2 2.372(7), In1–In4 2.8353(10), In2–N4 2.316(6), In2–N3 2.381(7), In2–In4 2.7557(9), In3–N6 2.348(6), In3–N5 2.471(6), In3–In4 2.7701(10), In4–In5 2.7619(9), In5–In6 2.7701(11), In6–N8 2.328(6), In6–N7 2.479(7); In2-In4-In5 118.06(3), In2-In4-In3 105.69(3), In5-In4-In3 126.13(3), In2-In4-In1 90.42(3), In5-In4-In1 103.32(3), In3-In4-In1 106.31(3), In4-In5-In6 121.07(3).

of binary indium sub-halides, which are all “saltlike” and possess no more than one In–In interaction per ionic unit (e.g. In_5Br_7 exists as $In^{I}_3[In^{II}_2Br_6]Br$).[1,14]

Recently, another complex containing an In_6 core, but incorporating bulky anionic β-diketiminate ligands, was reported by Hill et al.: $[\{In^{I}(nacnac)\}_4\{In^{II}I(nacnac)\}_2]$ (nacnac = $[\{(2,4,6\text{-}Me_3C_6H_2)NC(Me)\}_2CH]^-$).[15] They made the proposal, on the basis of DFT calculations, that the red-orange color of the complex originates from $\sigma\rightarrow\sigma^*$ transitions along a σ-delocalized linear In_6 chain. Although **1** does not have a linear metal chain, the similarity of its visible spectrum with that of $[\{In^{I}(nacnac)\}_4\{In^{II}I(nacnac)\}_2]$ ($\lambda_{max} = 348.9$ nm, $\varepsilon_{max} = 12810\ \text{M}^{-1}\text{cm}^{-1}$) prompted us to carry out DFT calculations on it. The geometry of the optimized gas-phase structure of **1** was found to be in close agreement with that of its crystal structure, but with slight overestimations of the In–In and In–I bond lengths (ca. 4 and 2%, respectively, for mean bond lengths). An orbital analysis revealed that the five indium–indium (σ-type) interactions are associated with the four highest occupied molecular orbitals (HOMOs, Figure 2).

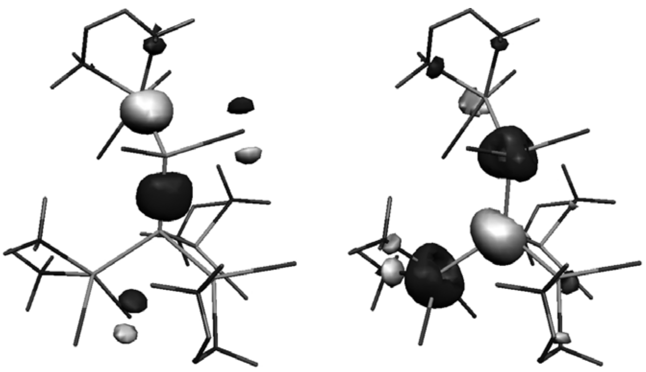

Figure 2. DFT (B3LYP) calculated HOMO (left) and LUMO (right) for **1**.

Immediately below these lie orbitals containing character belonging to various combinations of iodine lone pairs. The lowest unoccupied molecular orbital (LUMO, Figure 2) and LUMO+1 largely comprise In–In σ*-type interactions. As the HOMO–LUMO energy separation (equivalent to $\lambda = 382$ nm) corresponds almost exactly to the λ_{max} value of the visible absorption band of **1**, it is not unlikely that this absorption arises from a metal-based $\sigma\rightarrow\sigma^*$ transition, as has been proposed for $[\{In^{I}(nacnac)\}_4\{In^{II}I(nacnac)\}_2]$.[15] In this respect, a time-dependent DFT study of **1** confirmed that the HOMO to LUMO electronic transition is the major contributor to the computed visible absorption band of **1**.

In conclusion, the dissolution of InI in tmeda/toluene mixtures has been shown not to give an indium(I) iodide complex as previously reported,[11] but instead the first example of a neutral indium sub-halide cluster complex. This result has important implications for the widely utilized application of indium(I) halides in reactions employing coordinating solvents. When analyzing the outcome of such reactions, synthetic chemists should consider that the active component of the reaction mixture may not be an insoluble indium(I) halide, but alternatively a transient, “solubilized” indium sub-halide complex. In addition, given the fascinating field of chemistry that has arisen from aluminum and gallium sub-halide complexes, there is enormous scope to extend this preliminary study to the establishment of a similar area of chemistry dedicated to indium sub-halide complexes. Work towards this goal, and an examination of the synthetic applicability of **1**, continues in our laboratory.

Experimental Section

$[In_6I_8(tmeda)_4]$ (**1**): A mixture of toluene (3 mL) and tmeda (0.37 mL, 2.48 mmol) was added to solid InI (0.30 g, 1.24 mmol) at −80 °C. The suspension was allowed to warm slowly to room temperature with stirring to afford a red-orange solution. Filtration and slow cooling of the filtrate to −30 °C yielded red-orange crystals of **1**·(toluene)$_3$ (0.28 g, 75%); m.p. 66 °C (decomp. ca. 80 °C); . ^{1}H NMR (200 MHz, C_6D_6, 298 K, vacuum dried sample): $\delta = 1.72$ (br s, 16 H, (NCH_2), 2.01 ppm (br s, 48 H, (NCH_3); ^{13}C{^{1}H} NMR (37.8 MHz, C_6D_6, 298 K): $\delta = 46.1$ (NCH$_3$), 55.6 ppm (NCH$_2$); IR $\tilde{\nu} = 735$ (s), 948 (s) 1007 (m), 1024(s), 1048(m), 1102 (m), 1167 (m), 1237 (m), 1378 (s), 1462 (s), 1601 cm^{-1} (m); MS/EI *m/z* (%) 484.9 ($[InI_2(tmeda)]^+$, 6), 368.7 ($[InI_2]^+$, 100), 241.8 ($[InI]^+$, 97); UV/Vis λ_{max} (toluene, 7.6×10^{-5} M) = 381.0 nm ($\varepsilon_{max} = 10410\ \text{M}^{-1}\text{cm}^{-1}$); analysis calcd (%) for $C_{45}H_{88}I_8In_6N_8$: C 22.1, H 3.63, N 4.58; found: C 21.7, H 3.90, N 4.65. Crystallographic data for **1**·(toluene)$_3$: $C_{45}H_{88}I_8In_6N_8$, $M_r = 2445.35$, monoclinic, $P2_1/c$, $a = 12.131(2)$, $b = 11.678(2)$, $c = 51.078(10)$ Å, $\beta = 91.93(3)°$, $V = 7232(2)$ Å^3, $Z = 4$, $\rho_c = 2.246$ Mg m^{-3}, $T = 123(2)$ K, $\lambda = 0.71073$ Å. 24403 reflections collected, 14110 independent [R(int) = 0.0375], which were used in all calculations. $R_1 = 0.0434$, $wR_2 = 0.0908$ for observed unique reflections [$F^2 > 2\sigma(F^2)$] and $R_1 = 0.0803$, $wR_2 = 0.1042$ for all unique reflections. Max. and min. residual electron densities 1.44 and −1.25 e Å^{-3}. CCDC 657508 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Full details and references for the DFT calculations on $[In_6I_8(tmeda)_4]$, a representation of the UV/Vis spectrum of $[In_6I_8(tmeda)_4]$, and crystallographic information for $[In_2I_4(tmeda)_2]$·(toluene) (CCDC 657507) can be found in the Supporting Information.

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