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Controlled Decomposition of an Indium Trihydride Adduct: Synthesis and Characterization of the First Mixed-Oxidation-State Indium Sub-halide Complex Anion, $[In_5Br_8(quinuclidine)_4]^-$

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The first example of a compound containing a mixed-oxidation-state indium sub-halide complex anion, $[In_5Br_8(quinuclidine)_4]^-$, has been accessed by the controlled decomposition of an indium trihydride adduct, $[InH_3(quinuclidine)]$, in the presence of LiBr. An intermediate in this reaction, $[InH_2Br(quinuclidine)_2]$, has been isolated and suggests that its mechanism involves hydride–bromide exchange, reductive dehydrogenation, and disproportionation processes.

The chemistry of polyhedral and nonpolyhedral complexes of aluminum and gallium sub-halides has rapidly expanded in recent years.[1] The advances made in this field have mainly come from the group of Schnöckel, who have developed a specialized reactor to generate metastable metal(I) halide complexes of the type $[\{MX(L)\}_n]$, where M = Al or Ga, X = Cl, Br, or I, and L = ether, amine, or phosphine. The controlled decomposition of these halides has led to an array of clusters and related complexes in which the average oxidation state of the metal is either greater than or less than +1, e.g., $[Al_{22}Cl_{20}(THF)_{12}]$,[2] $[Al_5Br_6(THF)_6]^+[Al_5Br_8(THF)_4]^-$,[3] $[Ga_{24}Br_{22}(THF)_{10}]$,[4] and $[Ga_5Cl_7(OEt_2)_5]$.[5] It is of note that other lower nuclearity gallium sub-halide complexes have come from the partial disproportionation of "GaI" in the presence of Lewis bases.[6] Perhaps surprisingly, indium sub-halide cluster complex chemistry is nonexistent, though a variety of complexes of the type $[(L)X_2InInX_2(L)]^{n-}$, where L = Lewis base, X = halide, $n = 0$; L = X = halide, $n = 2$, are known,[7] as are a range of binary sub-halides, e.g., In_5Br_7 and In_4Br_7.[8] The latter of these are, however, generally "saltlike" and do not consist of discrete molecular units. It should also be mentioned that a number of alkyl-[9] or alkyl/halide[10]-substituted mixed-oxidation-state indium clusters and related compounds have been recently reported.

Part of the reason behind the paucity of indium sub-halide cluster complexes must come from the very low solubility of indium(I) halides in most organic solvents. In addition, it is reasonable to assume that indium(I) halides should be more stable toward disproportionation reactions than their lighter group 13 counterparts. It seemed to us that an alternative route to polynuclear indium sub-halide complexes could involve the controlled decomposition of thermally labile indium(III) species. In recent years, we have developed synthetic and stabilization strategies that have allowed us to access the first indium trihydride and related indium hydride complexes.[11] Although these can be exceptionally thermally stable, e.g., $[InH_3\{C[N(Mes)C(H)]_2\}]$, where Mes = mesityl (dec 115 °C), they normally decompose to indium metal, dihydrogen, and free ligand at close to room temperature. Herein, we report the remarkable controlled decomposition reaction of one of these, $[InH_3(quin)]$, where quin = quinuclidine, in the presence of LiBr, which has yielded the anionic indium sub-halide complex, $[H(quin)_2]^+[In_5Br_8(quin)_4]^-$.

It is known that pure samples of $[InH_3(quin)]$, prepared from $LiInH_4$ and quin·HCl, decompose in solution or in the solid state above −5 °C to give indium metal, H_2, and quinuclidine.[11,12] However, we observed that when an

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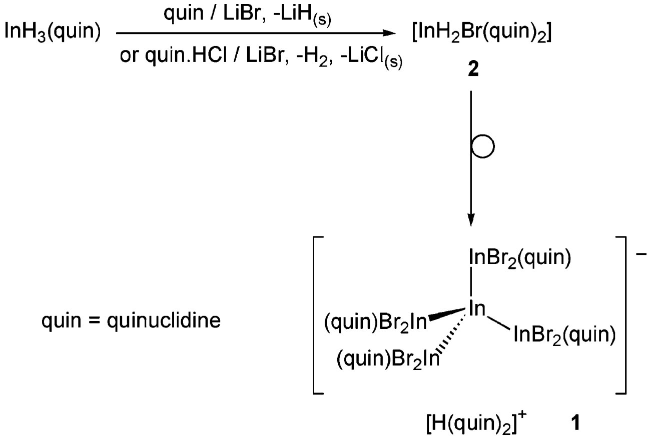
Scheme 1



unpurified diethyl ether reaction solution containing $[InH_3(quin)]$ and LiBr (an ether-soluble byproduct in the synthesis of $LiInH_4$ from LiH and $InBr_3$[11]) was stored at −30 °C, it took on a deep orange color over 5 days and some indium metal was deposited. Concentration of this solution afforded the complex $[H(quin)_2]^+[In_5Br_8(quin)_4]^-$ (**1**, <5%; Scheme 1), which is closely related to both the salt, $[Al_5Br_6(THF)_6]^+[Al_5Br_8(THF)_4]^-$,[3] and the neutral complex, $[Ga_5Cl_7(OEt_2)_5]$.[5] Concentration of another such reaction solution after standing for only 2 days at −30 °C gave the new colorless crystalline complex $[InH_2Br(quin)_2]$ (**2**), in low yield, again with some indium metal deposition. These observations prompted an investigation of the mechanisms of the unusual reactions that yielded **1** and **2**.

It seemed that **2** could possibly be an intermediate in the formation of **1** and may have been formed via a bromide−hydride exchange reaction between $[InH_3(quin)]$ and LiBr. The second-coordinated equivalent of quinuclidine in **2** likely arises from the full decomposition of some $[InH_3(quin)]$ in the solution, as evidenced by the deposition of indium metal. To test these hypotheses, solutions of pure $[InH_3(quin)]$ or **2** were treated with anhydrous LiBr (20 equiv) and placed at −30 °C for 5 days. In both cases, orange solutions resulted and **1** could be isolated in low yield. It seems, therefore, that the mechanism of formation of **1** does involve initial hydride−bromide exchange reactions to give $[InH_2Br(quin)_{1or2}]$ and perhaps $[InHBr_2(quin)_{1or2}]$, though we have no evidence for the presence of any dibromide complex as yet. These exchange reactions are presumably driven by the insolubility of the LiH product relative to the LiBr reactant. In this respect, we have recently shown that anion−hydride exchange and subsequent alkali-metal hydride deposition processes involving $[InH_3(quin)]$ can be facile.[13] Both $[InH_2Br(quin)_{1or2}]$ and $[InHBr_2(quin)_{1or2}]$ could then undergo homolytic In−H cleavage reactions (H_2 elimination) and a subsequent series of partial disproportionation/comproportionation and bromide transfer reactions to give the anion, $[In_5Br_8(quin)_4]^-$ (cf. the formation of $[Al_5Br_8(THF)_4]^-$ [3]). The proton of the $[H(quin)_2]^+$ cation probably results from a solvent abstraction process, which is reasonable considering the likely presence of highly reactive transient intermediates, e.g., radicals, in the reaction solution. There is a recent precedent for the generation of such radicals from a complex closely related to $[InHBr_2(quin)_{1or2}]$, viz., $[InHCl_2(THF)_n]$, which has been shown to reduce alkyl halides at room temperature via a process involving $^{\bullet}InCl_2$ radicals as intermediates.[14] In addition, $[GaHCl_2(L')_2]$, where L′ = 3,5-dimethylpyridine, has been reported to undergo a reductive dehydrogenation reaction to give $[(L')Cl_2Ga^{II}Ga^{II}Cl_2(L')]$ in boiling toluene, presumably via homolytic Ga−H bond cleavage.[15]

A more rapid route to **2** was devised whereby an in situ generated ethereal solution of $LiInH_4$/LiBr was treated with 2 equiv of quin·HCl.[16] Placement of the reaction mixture overnight at −30 °C gave a 24% isolated yield of the complex. When the reaction was repeated but left at −30 °C for 3 days, an orange solution resulted, which upon workup gave **1** in a 17% yield. This alternate route circumvents the initial hydride−bromide exchange reaction, thus leading to the accelerated reaction times. The low but reproducible yield of **1** from both synthetic pathways suggests that the deeply colored reaction solutions contain other indium sub-halide species. None of these have yet been isolated in a pure form despite repeated attempts.

Complex **1** is thermally unstable in solution above −15 °C, or in the solid state above 5 °C, and decomposes via disproportionation to give indium metal and $[InBr_3(quin)_2]$, among other products. Although **2** decomposes in solution at temperatures greater than −5 °C, it does not decompose rapidly in the solid state until 72 °C, though it slowly (over 3 days) deposits indium metal upon standing at 25 °C. Both compounds are diamagnetic, though little information could be obtained from their ^1H NMR spectra. These display broad signals resulting from the quinuclidine ligands, which did not resolve in the temperature range from −20 to −50 °C. The ^1H NMR spectrum of **2** does, however, exhibit a characteristically broad hydride signal centered at δ 3.56 ppm, which is in the normal region for indium hydride

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(16) Experimental data for **1**: To an in situ generated solution of $LiInH_4$ (1.41 mmol) containing ca. 4.2 mmol of LiBr in diethyl ether (60 cm^3) at −78 °C was added solid quin·HCl (0.42 g, 2.81 mmol) over 5 min. The resultant colorless suspension was warmed to −30 °C, stirred for 2 h, filtered, and kept at this temperature for 72 h to yield an orange solution. Volatiles were removed in vacuo and the residue extracted into toluene (15 cm^3). Placement at −50 °C overnight yielded **1** as yellow-orange prisms (0.09 g, 17% based on indium); mp 5−6 °C (dec); ^1H NMR (400 MHz, $C_6D_5CD_3$, 243 K) δ 1.89 (br m, 36 H, CH_2), 2.19 (br m, 6 H, CH), 3.26 (br m, 36 H, CH_2N), NH resonance not observed; IR ν/cm^{-1} (Nujol) 2580 v br (N−H), 1318 m, 1047 s, 981 s, 826 m, 791 m, MS/APCI *m/z* (%): 112 [quinH$^+$, 100]. Experimental data for **2**: reaction conditions as for **1** except the ether reaction solution was concentrated to 5 cm^3 immediately after filtration and placed at −30 °C for 8 h to yield **2** as colorless prisms (0.14 g, 24%); mp 72−74 °C (dec); ^1H NMR (300 MHz, $C_6D_5CD_3$, 243 K) δ 1.29 (br m, 12 H, CH_2), 1.49 (br m, 2 H, CH), 2.79 (br s, 12 H, CH_2N), 3.56 (br s, 2 H, InH); ^{13}C NMR (100.6 MHz, $C_6D_5CD_3$, 243 K) δ 26.6 (CH), 30.4 (CH_2), 47.8 (NCH_2); IR ν/cm^{-1} (Nujol) 1707 (br s, In−H); MS/APCI *m/z* (%) 112 [quinH$^+$, 100]. Reproducible microanalyses could not be obtained for **1** or **2** because of their high air sensitivity and thermal instability at 25 °C. The low solubility of **1** at 243 K in $C_6D_5CD_3$ precluded the acquisition of interpretable ^{13}C NMR data for this compound.

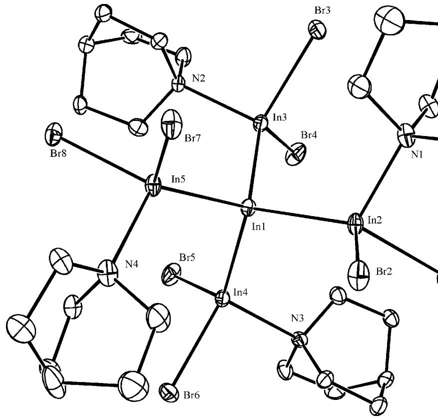

Figure 1. Structure of the anionic component of **1**. Selected bond lengths (Å) and angles (deg): In1−In2 2.7460(14), In1−In3 2.7471(14), In1−In4 2.7484(14), In1−In5 2.7451(13), In2−N1 2.260(13), In3−N2 2.297(11), In4−N3 2.298(11), In5−N4 2.268(14), In2−Br1 2.5652(19), In2−Br2 2.5519(19), In3−Br3 2.588(2), In3−Br4 2.565(2), In4−Br5 2.566(2), In4−Br6 2.586(2), In5−Br7 2.5534(19), In5−Br8 2.5663(19), In2−In1−In3 110.19(4), In2−In1−In4 112.42(5), In2−In1−In5 110.02(4), In5−In1−In3 112.47(5), In5−In1−In4 110.07(4).

species.[11] In addition, a strong, broad In−H stretching absorption is present in its infrared spectrum at 1707 cm^{-1}. This is at a significantly higher wavenumber than is normal for indium trihydride complexes, e.g., [InH_3(quin)] at 1642 cm^{-1},[12] because of a negative inductive effect from the bromide ligand, which reduces the polarity of the In−H bonds relative to those in InH_3 complexes.

Complex **1** was crystallographically characterized,[17] and the structure of its anionic component is depicted in Figure 1. This shows it to have a central indium atom tetrahedrally coordinated by four $InBr_2$(quin) fragments. A very similar arrangement has been seen for the M_5 fragments in the anion, $[Al_5Br_8(THF)_4]^-$, and the neutral complex, $[Ga_5Cl_7(OEt_2)_5]$, which, as in **1**, have formal average metal oxidation states of 1.4. The average In−In bond length in **1** (2.747 Å) is shorter than the mean for all crystallographically characterized examples (3.02 Å)[18] but similar to those in related homoleptic complexes, e.g., 2.696(2) Å in $[In\{In(Trip)_2\}_3]$, where Trip = $C_6H_2Pr^i_3$-2,4,6.[19] Its In−N and In−Br bond lengths are in the normal range, and its cationic component, which has no significant contact with the anion, has been previously structurally characterized.[20] Complex **2** (Figure 2) is isomorphous with both its aluminum and gallium analogues, $[MH_2Cl(quin)_2]$, where M = Al[21] or Ga,[22] and represents the first structurally characterized tertiary amine adduct of an indium hydride fragment. Its crystallographically independent hydride ligand was located from difference maps and refined isotropically without restraints. This shows the geometry of the indium center to be distorted trigonal bipyramidal with the quinuclidine ligands in axial positions. The In−H distance [1.60(5) Å] compares well with those in the few other crystallographically authenticated indium hydride complexes.[11] All other geometric parameters within this complex are unexceptional.

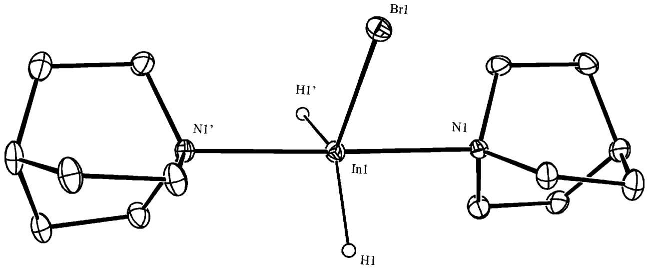

Figure 2. Molecular structure of **2**. Selected bond lengths (Å) and angles (deg): In1−N1 2.429(3), In1−Br1 2.5930(8), In1−H1 1.60(5), N1−In1−N1′ 178.03(14), H1−In1−Br1 113.7(17), H1−In1−H1′ 132.6(5), Br1−In1−N1 89.02(7), H1−In1−N1 90.0(17). Symmetry operation ′: $-x$, y, $-z + {}^1/_2$.

In conclusion, we have devised an unusual synthetic route to the first example of a mixed-oxidation-state indium sub-halide complex anion. This has involved the controlled decomposition of an indium trihydride adduct in the presence of LiBr. Although this reaction is relatively low-yielding and its mechanism is not yet fully understood, it is reproducible. This lends hope to the possibility of utilizing similarly controlled indium hydride decomposition reactions in the preparation of a range of higher nuclearity indium sub-halide complexes and clusters that will be comparable to their now well-studied aluminum and gallium counterparts. We will report on our efforts in this direction in a later publication.

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Supporting Information Available: Crystallographic CIF files for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Crystal data for **1**: $C_{42}H_{79}Br_8In_5N_6$, $M = 1881.49$, hexagonal, space group $P3$, $a = b = 21.359(3)$ Å, $c = 15.206(3)$ Å, $V = 6007.7(17)$ Å^3, $Z = 3$, $D_c = 1.560$ g cm^{-3}, $F(000) = 2694$, μ(Mo Kα) = 5.433 mm^{-1}, $T = 150(2)$ K, 14 109 unique reflections [R(int) = 0.1067], R (on F) = 0.0711, R_w (on F^2) = 0.1724 ($I > 2\sigma I$). Crystal data for **2**: $C_{14}H_{28}BrInN_2$, $M = 419.11$, orthorhombic, space group $Pbcn$, $a = 11.215(2)$ Å, $b = 12.033(2)$ Å, $c = 12.634(3)$ Å, $V = 1705.0(6)$ Å^3, $Z = 4$, $D_c = 1.633$ g cm^{-3}, $F(000) = 840$, μ(Mo Kα) = 3.718 mm^{-1}, $T = 150(2)$ K, 1950 unique reflections [R(int) = 0.0513], R (on F) = 0.0321, R_w (on F^2) = 0.0623 ($I > 2\sigma I$).

(18) As determined from a survey of the Cambridge Crystallographic Database, Mar 2005.

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