Ambient-Temperature Formation of Crystalline Indium Monohalides from Aqueous Media

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The chemistry of some fundamental compounds of indium, such as simple halides, is still worth studying although the first investigations go back to the early work of Nilson and Pettersson[1] and of Thiel,[2] having brought to light their synthesis and chemical behavior. Thiel reported the pronounced chemical instability of low valent indium such that, to give an example, ordinary water decomposes white indium dibromide $InBr_2$ ($\equiv In$-$[InBr_4]$) into soluble white indium tribromide $InBr_3$ and apparently insoluble red indium monobromide $InBr$, the latter immediately decaying into the tribromide and inert elemental indium.

The structural chemistry of the indium bromides is exceptionally rich because of the various mixture ratios in which In^+, In^{2+}, and In^{3+} may combine with each other in the solid state. There can be no doubt about the existence of $InBr$,[3] In_5Br_7 ($\equiv InBr_{1.4}$),[3,4] In_2Br_3 ($\equiv InBr_{1.5}$),[3,5] $InBr_2$,[3,6] and $InBr_3$[3] but it is not clear at present whether or not the phase In_4Br_7 ($\equiv InBr_{1.75}$), indicated by two independent investigations,[7,8] does, in fact, exist. In the following we report on a new reaction giving access to the most reduced of all indium bromides, $InBr$, and the corresponding chloride and iodide.

## Solubility of Indium in Hydrohalic Acids

In the course of preparing InX_3 ($X = Cl, Br, I$), we have made an unexpected observation upon dissolving elemental In in hydrohalic acids. The aqueous solutions of HCl, HBr, and HI (all Merck, p.a.) had exact normalities of 11.99, 9.07, and 7.87 N, measured by titration with standard 1.003 M NaOH solution (Aldrich) against bromothymol blue. According to the textbook equation

$$In(s) + 3H^+(aq) = In^{3+}(aq) + \tfrac{3}{2}H_2 \qquad (1)$$
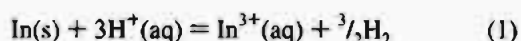
10 mL of each of the above specified solutions of HCl, HBr, and HI can not dissolve more than 4.59 g (40.0 mmol), 3.47 g (30.2 mmol), and 3.01 g (26.2 mmol) of metallic indium, respectively. When stirring them at about 50 °C for one day, however, quantities of 5.30, 4.04, and 3.75 g In are easily brought into solution (measured by weighing of the excess In), corresponding to an excess-solubility of In in these solutions of more than 15, 16, and 24% for HCl, HBr, and HI, respectively.

An exemplary photograph of such an In-saturated HBr solution is shown in the left part of Figure 1. Besides the
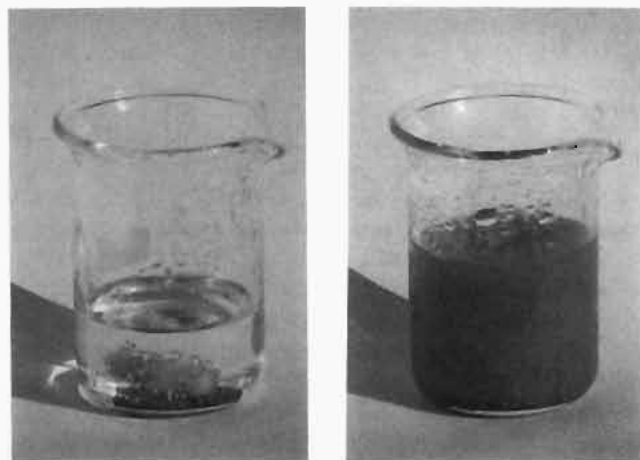

Figure 1. *Left*: An indium-saturated aqueous solution made from concentrated hydrobromic acid (9.07 N) and metallic indium after 24 h of stirring at 50 °C. The solution is characterized by a slight yellowish/greenish color whereas the indium metal sediment shows a brass-like color. *Right*: The same solution after dilution up to twice the volume using demineralized water; generation of molecular hydrogen and precipitation of InBr occur spontaneously.

solution's slight yellowish/greenish color it is important to notice the brass-like color of the indium metal sediment (pure In has a silvery look), a clear sign that the metal surface is involved in a chemical reaction. Interestingly, the pH value[9] does not exceed 0.5, *i.e.* only about 97% of all formerly available protons have been reduced to molecular hydrogen.

Since more indium is dissolved than what can be expected from eq 1, lower valent indium cations *must* be present in solution. Unfortunately, low valent indium chemistry in acidic water is difficult to investigate since lower oxidation states of In are fairly unstable below pH 7, and $In(OH)_3$ is known to precipitate above pH 3. Despite these problems, Hepler et al.[10] as well as Biedermann and Wallin[11] proved that there is an equilibrium such as

$$2In(s) + In^{3+}(aq) = 3In^+(aq) \qquad (2)$$
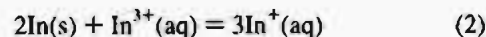
by determining its equilibrium constant in dilute (<0.2 M) perchlorate solution. Both groups, however, differ in the existence of the other possible equilibrium

$$In(s) + 2In^{3+}(aq) = 3In^{2+}(aq) \qquad (3)$$
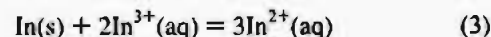
Indeed, all other investigations are in accord in stating that In^{2+} is extremely unstable after having been generated (<0.1 M),[12–14] and it decays by disproportionation in the millisecond time range following

$$2In^{2+}(aq) = In^{3+}(aq) + In^+(aq) \qquad (4)$$
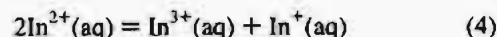
by neither a simple first nor second order rate law.[14]

We have investigated the above mentioned solution by means of electron pulse resonance (EPR) technique with field strengths

(1) Nilson, L. F.; Pettersson, O. *Z. Phys. Chem.* **1888**, *2*, 657.
(2) Thiel, A. *Z. Anorg. Chem.* **1904**, *40*, 280. Specifically, we owe to Thiel the knowledge about the awful ink-like taste of indium trichloride, $InCl_3$.
(3) Staffel, T.; Meyer, G. *Z. Anorg. Allg. Chem.* **1987**, *552*, 113; **1988**, *563*, 27.
(4) Marsh, R. E.; Meyer, G. *Z. Anorg. Allg. Chem.* **1990**, *582*, 128.
(5) Bärnighausen, H. *Z. Kristallogr.* **1989**, *186*, 16.
(6) Beck, H. P. *Z. Naturforsch.* **1987**, *42b*, 251.
(7) Walter, P. H. L.; Kleinberg, J.; Griswold, E. *J. Inorg. Nucl. Chem.* **1961**, *19*, 223.
(8) Morawietz, W.; Morawietz, H.; Brauer, G. *Z. Anorg. Allg. Chem.* **1962**, *316*, 220.

(9) Calibrated digital glass electrode Conducta PM 9, type 7120-GS.
(10) Hepler, L. G.; Hugus, Z. Z., Jr.; Latimer, W. M. *J. Am. Chem. Soc.* **1953**, *75*, 5652.
(11) Biedermann, G.; Wallin, T. *Acta Chem. Scand.* **1960**, *14*, 594.
(12) High-energy electron pulse radiolysis of In(III) perchlorate solutions was done by Taylor, R. S.; Sykes, A. G. *J. Chem. Soc. A* **1969**, 2419.
(13) Sukhov, N. L.; Makarov, I. E.; Ershov, B. G. *Khim. Vys. Energ.* **1978**, *12*, 375.
(14) Schwok, A. S.; Rabani, J. *Radiat. Phys. Chem.* **1984**, *23*, 211. Low valence In solutions might have a potential use as an intermediate in H_2 generation by water reduction in photochemical and radiation chemical systems.

between 1000 and 5000 G, and we could not find any indication of an unpaired spin.[15] This definitely excludes the presence of In^{2+} although species such as $In_2Br_6^{2-}$, containing divalent In but having the remaining electron spin-paired in the In^{2+}-In^{2+} bond,[3,4,16] might still be possible.

On the basis of 10 mL of 9.07 N HBr solution, the remaining proton concentration of about $10^{-0.5}$ M $\approx$ 0.316 M, and the amount of dissolved indium (4.04 g), a simple calculation using eqs 1 and 2 shows that the indium-saturated solution contains indium concentrations of approximately

$$c(In^{3+}) = 2.62 \text{ M and } c(In^+) = 0.90 \text{ M}$$

This goes far beyond the typical concentrations of In^+ already reported (3×10^{-4} M and 2.5×10^{-5} M), generated by indium anodization in perchlorate solution[12,17] as a prerequisite for In^+ redox reactions.[18] Nearly all investigations concerning In^{3+} in aqueous media were limited to typical concentrations of about 10^{-3} M, with the exception of two papers (up to 0.75 M).[11,19] The difference in concentrations of In^+ between the present work and the literature is by no means a contradiction: previous research was focused mainly on the need to interpret UV spectra (200–400 nm), thus restricting concentrations to very low values.[20] Our own attempts in collecting UV spectra were unsuccessful in so far as the solution begins to absorb strongly below 420 nm and is completely opaque for UV radiation below 350 nm.[21] This is especially unfortunate since the extinction parameters for In^+, In^{2+}, and In^{3+} are available.[12]

We have not observed any apparent decomposition of the solution over a time period of several hours and it is quite stable even at a temperature of 50 °C in an open beaker. The possible decay of In^+ according to

$$In^+(aq) + 2H^+(aq) = In^{3+}(aq) + H_2 \qquad (5)$$
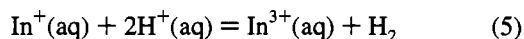
accompanied by the generation of molecular hydrogen[17] is seemingly hindered because of kinetic reasons (note that pH still lies around 0.5). At temperatures above 60 °C, however, $InBr_3$ begins to precipitate.

Precipitation of InBr

To our surprise, however, the aqueous indium-saturated HBr solution is *astonishingly unstable when diluted with water*—partial decomposition occurs. The right side of Figure 1 shows the spontaneous precipitation of an orange-red material when the solution is diluted with hot or cold demineralized water, accompanied by the formation of a colorless gas. Interestingly, although the metal sediment is imperative for the generation of above specified solution containing In^{3+} and In^+, the reaction discovered here is completely independent of the presence of

excess metallic In. Even after having *decanted* the solution from indium, the precipitation reaction occurs *exactly* in the same way.

The precipitate, almost pure indium monobromide InBr, could be filtered from the solution, washed with the mother liquid, and dried over silica gel in vacuum. When stored in dry air, no sign of decomposition whatsoever was detected over several months. X-ray powder diffraction confirms the T/I structure type, and the refined lattice constants (34 reflections, Si-calibrated STOE powder diffractometer, 25 °C) are $a = 446.40$-(3) pm, $b = 1236.49(6)$ pm, and $c = 473.94(4)$ pm, in excellent agreement (standard deviation 0.02%) with the most accurate previous investigation.[22]

The reaction is more carefully set in motion whenever a single water drop falls onto the solution's surface. Over minutes the simultaneous growth of plate-like orange-red *single crystals* of InBr (up to 1 mm in size) and the appearance of tiny gas-bubbles can be observed. According to X-ray investigations (precession technique), the single crystals are of excellent quality, and their main face is the (010) face.

To the best of our knowledge, spontaneous precipitation of InBr from aqeous solution by dilution has never been reported. On the contrary, InBr and the other bromides are more typically prepared via higher-temperature routes (300–400 °C) from the elements,[8] from In and $HgBr_2$,[23] or from synproportionation of In and $InBr_3$.[24] In some sense, the reaction is a beautiful example for *chimie douce*,[25,26] *i.e.*, making solid state syntheses work at moderate temperatures.[27] Unfortunately, in contrast to what might be anticipated from Figure 1, the yield of InBr produced in the (unoptimized) reaction here does not exceed 3% with respect to the amount of dissolved indium. It is probably not appropriate for large scale syntheses but it is well-suited for growing crystals for X-ray diffraction purposes. There may also be some potential for synthesis of ternary compounds. All the remaining indium in the mother liquid can still conventionally be extracted from it as $InBr_3$.

Mechanistic Considerations

In order to explain the mechanism of InBr precipitation one has to focus both on the astonishing stability of In^+ in solution and the InBr formed (note that textbooks claim In(I) compounds to be unstable in water, referring back to Thiel) and on the nature of the gas released.

There are two beautiful investigations by Red'kin et al.,[28,29] probably not too extensively noticed by the community, proving that small amounts of previously synthesized, finely powdered InBr can indeed be dissolved in strictly deoxygenated water at room temperature provided that stirring is extremely *fast*; the highest concentrations were about $7-10 \times 10^{-3}$ M. Thus, there is considerable stability under appropriate conditions although

(15) The sample was filled into a quartz glass capillary (outer $\phi = 2$ mm, inner $\phi = 1$ mm) and scanned in the X band range ($\gamma = 9.52$ GHz) with a modulation between 20 and 2 Gpp and attenuation between 10 and 30 dB.

(16) Freeland, B. H.; Hencher, J. L.; Tuck, D. G.; Contreras, J. G. *Inorg. Chem.* **1976**, *15*, 2144.

(17) Visco, R. E. *J. Phys. Chem.* **1965**, *69*, 202.

(18) Kinetic studies on the reaction of In^+ with Fe^{3+}, I_3^-, and O_2 in aqueous solution were first published by: Taylor, R. S.; Sykes, A. G. *J. Chem. Soc. A* **1971**, 1628.

(19) Biedermann, G.; Ferri, D. *Acta Chem. Scand. A* **1982**, *36*, 611. Within perchlorate solutions of In^{3+} (0.2–0.75 M) two polynuclear ions (In_2-$(OH)_2^{4+}$ and $In_4(OH)_6^{6+}$) were observed, being in equilibrium via In^{3+} ions.

(20) The exclusive choice of perchlorate media can be understood in the necessity to keep the ionic strength at almost constant values.

(21) We have used a Perkin-Elmer Lambda 9 spectrometer (halogen lamp, photomultiplier) and scanned through a solution which was 5 mm thick.

(22) Meyer and Staffel have reported almost as precise lattice constants for InBr: $a = 446.6(1)$ pm, $b = 1236.8(2)$ pm, and $c = 473.9(1)$ pm.[3]

(23) Clark, R. J.; Griswold, E.; Kleinberg, J. *J. Am. Chem. Soc.* **1958**, *80*, 4764.

(24) Klemm, W.; Dierks, F. *Z. Anorg. Allg. Chem.* **1934**, *219*, 42.

(25) Rouxel, J. *Chem. Scr.* **1988**, *28*, 33.

(26) Figlarz, M. *Chem. Scr.* **1988**, *28*, 3.

(27) Two related examples for low-temperature syntheses of reduced In(I) compounds in strictly anhydrous refluxing organic media such as acetonitrile: Ashraf, M.; Aziz-Alrahman, A. M.; Headridge, J. B. *J. Chem. Soc. Dalton Trans* **1977**, 170; Freeland, B. H.; Tuck, D. G. *Inorg. Chem.* **1976**, *15*, 475.

(28) Polarographic investigation by: Red'kin, A. N.; Dubovitskaya, L. G.; Smirnov, V. A. *Zhur. Neorg. Khim.* **1982**, *27*, 627.

(29) Red'kin, A. N.; Dubovitskaya, L. G.; Smirnov, V. A.; Dmitriev, V. S. *Zhur. Neorg. Khim.* **1985**, *30*, 620. Moist InBr is slightly photosensitive.

the In(I) concentration was still two orders of magnitude smaller than in the present solution. Nonetheless the Russian group's claim that decomposition of dissolved InBr occurs within 15 min at 50 °C was not confirmed here. Probably In$^+$ can not decompose into In^{3+} since the latter is already *fully concentrated* in solution. Also, although precipitation of InBr was observed by Red'kin et al. upon cooling the solution (exceeding the solubility product) we again stress that in the much more enriched solution here precipitation of InBr occurs under *opposite* circumstances, namely by *dilution*.

To specify the unknown gas, we have repeated the experiment in a strictly closed apparatus starting with 40 mL degassed HBr solution (via ultra-sound treatment) and the appropriate amount of indium; Argon was used as a protecting gas. Gas samples were collected by filling evacuated 20 mL Schlenk containers with the atmosphere from the apparatus *before* and *after* InBr precipitation had been initiated by degassed and demineralized water. Finally, mass spectroscopic measurements were performed at a pressure of $p = 9.6 \times 10^{-6}$ mbar.[30]

Practically no difference in the composition of the two gas samples could be found with respect to Ar and trace gases (H_2O, N_2, O_2) while the colorless gas was identified to be molecular hydrogen. However, the increase in its concentration was by more than 80% due to the deuterium isotope species of mass 3, namely ^1H-^2H. To give an estimate, we have collected about half of the HD amount that can be principally set free from the HBr solution if deuterium ^2H is present in its natural abundance of 0.015%.[31] This does not mean that the deuterium can be traced back to originate from HBr since protons and deuterons from the HBr molecule and the water solvent are indistinguishable (rapid exchange). We have no explanation for this pronounced isotope effect although it is justifiable to assume that deuterium is enriched in the solution upon indium dissolution (similar to what happens during water electrolysis), and finally set free by the precipitation reaction.

Because of the H$^+$ (D$^+$) reduction, there must be oxidation of another species while InBr precipitation starts. Thus, in this respect In^{3+} can be excluded from consideration (it can only be reduced); on the other hand, neutral solvated In^0 is extremely unlikely to be present in solution. One either has to assume other species to be involved or the precipitation to be a reaction *following* a starting oxidation.

We do not dare to assume that water is oxidized to release molecular hydrogen; the bromine anions present would definitively be easier to oxidize on the basis of tabulated standard potentials.[31] It seems more logical to focus on the *hydrolysis* of the main species In^{3+} according to a diffusion-controlled process[32] that follows

$$InX^{2+}(aq) + H_2O = InOH^{2+}(aq) + H^+ + X^- \quad (6)$$
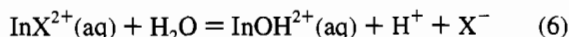
in concentrated[33] solutions, finally leading to polynuclear cluster species.[19,34] Addition of excess water would drive eq 6 to the right side. The resulting *additional* protons would be followed by a depletion of In$^+$ since its decay to In^{3+} according to eq 5 could start (the solution becomes (*i*) more acidic and (*ii*) more

diluted such that In^{3+}(aq) may form), releasing molecular hydrogen that has been recognized macroscopically. *This would also perfectly match our observation that the solution's pH does not change significantly upon precipitation.* Moreover, we know[28] of the existence of a complex designated In$_2$Br$^+$ whose equilibrium with In$^+$ can be formulated to be

$$In_2Br^+(aq) = InBr(s) + In^+ \quad (7)$$
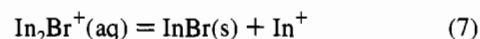
In this way the decay of In$^+$, started through In^{3+} hydrolysis, would pull the last equilibrium to the right side, releasing InBr *in situ* such that InBr precipitation may happen as a second-step reaction due to the supersaturation of InBr (comparatively small solubility product, maximum InBr concentration around $7-10 \times 10^{-3}$ M).[28] However, the proposed precursor In$_2$Br$^+$ might not be the only monovalent precursor to InBr.

Precipitation of InCl and InI

We have tried to find a similar precipitation reaction yielding indium chloride and indium iodide. For solutions of In in aqueous HCl, one first observes the spontaneous formation of red crystals at lower In$^+$ concentrations and then, at higher concentrations, the formation of yellow crystals upon careful addition of water. Isolation of the red crystals proves them to be X-ray amorphous while the yellow crystals decompose within seconds to yield metallic indium. Note that InCl is reported to exist in a red high-temperature phase (T/I type) and a yellow low-temperature phase[35] which would perfectly match Ostwald's step rule in this context, too. After 24 h of reflux stirring, however, a solution of indium in aqueous HCl transforms into a very thick, colorless paste which is almost impossible to stir anymore. When filtered over a dry-ice cooled glass frit, a yellow viscous oil can be extracted which, upon reaching room temperature, decomposes even under dried paraffin oil, followed by the formation of a gray metallic material (indium).

An indium-saturated solution of aqueous HI also shows a slight tendency to precipitate InI when treated with additional water. The formation of significant InI amounts is possible via dry-ice cooled filtration of the solution resulting in a red-violet powder material, together with sporadic single crystals here and there. Concerning its stability, InI resembles much more InBr than InCl does.

We think that the pronounced differences in monohalide precipitation (InBr very easily, mostly through dilution (chemical process); InI less easily, mostly through super-saturation by cooling; InCl least easily, followed by rapid decay) can be traced back to the availability of a promising precursor in solution; at the moment, a species such as In$_2$X$^+$ has been detected only in the bromide case. This is especially reasonable since the varying precipitation tendencies can not be explained by differences in lattice energies U such that the compound with the largest U precipitates most easily. On the contrary, approximate lattice energy calculations according to Kapustinskii's equation,[36] based on ionic radii for coordination number six,[31] show U(InCl) to be *larger* than U(InBr) by about 28 kJ/mol, and U(InBr) to be

(30) The accelerating voltage used was 1.1 kV (90 eV electron energy, 0.5 V/cm sensitivity). All gas peaks were corrected for relative ionization factors.

(31) Emsley, J. *The Elements*, 2nd ed.; Clarendon Press: Oxford, England, 1991.

(32) Investigations on the hydrolysis of dilute aqueous In^{3+} perchlorate solutions by the electric field jump relaxation method were performed by: Hemmes, P.; Rich, L. D.; Cole, D. L.; Eyring, E. M.; *J. Phys. Chem.* **1970**, *74*, 2859.

(33) Hepler, L. G.; Hugus, Z. Z., Jr. *J. Am. Chem. Soc.* **1952**, *74*, 6115.

(34) NMR investigations on ^{113}In and ^{115}In nuclei have demonstrated the strong tendency of In^{3+} to bind up to six water molecules: Buslaev, Yu. A.; Tarasov, V. P.; Buslaeva, M. N.; Petrosyants, S. P. *Dokl. Akad. Nauk. SSSR* **1973**, *209*, 882. Cationic or even neutral species such as InBr^{2+}, InBr$_2^+$, and InBr$_3$ but no anionic complexes were detected via Raman measurements in aqueous perchlorate solution: Hanson, M. P.; Plane, R. A. *Inorg. Chem.* **1969**, *8*, 746. In the chloride system, the species are InCl^{2+}, InCl$_2^+$, and InCl$_4^-$; see also: Dobud, P.; Lee, H. M.; Tuck, D. G. *Inorg. Chem.* **1970**, *9*, 1990.

(35) van der Vorst, C. P. J. M.; Verschoor, G. C.; Maaskant, W. J. A. *Acta Crystallogr. B* **1978**, *34*, 3333.

(36) Kapustinskii, A. F. *Q. Rev.* **1956**, *10*, 283.

larger than U(InI) by approximately 40 kJ/mol, counterintuitive to the experimental precipitation ordering. One still has to recognize that such a primitive calculation may underestimate the influence of the fairly short In^+-In^+ contact within the T/I structure type.[37]

Powder X-Ray Investigations

Careful examination of the powder pattern reveals eight *additional* diffraction peaks which do neither coincide with those of the five unambiguously characterized indium bromides nor with those of the oxides (α- and β-In_2O_3), hydroxides (InOOH, $In(OH)_3$), oxybromide (InOBr), or metallic indium. In any case, the presence of oxygen within the precipitate is very unlikely, its O content being possibly zero but at least smaller than the instrumental (AES) resolution of 0.3 weight per cent.

An index proposal yields an orthorhombic cell having lattice dimensions of $a = 489.9(2)$ pm, $b = 818.8(4)$ pm, and $c = 962.8(2)$ pm, giving a cell volume of 386.21 Å^3. If one assumes the additional phase to be another, so far unknown indium bromide, a comparison between *reduced* unit cell volumes of the bromides reveals an interesting relationship; they are for InBr: 65.44 Å^3, $InBr_{1.4}$ ($\equiv In_5Br_7$): 80.96 Å^3, $InBr_{1.5}$ ($\equiv In_2Br_3$): 86.48 Å^3, $InBr_2$: 108.07 Å^3, and $InBr_3$: 122.22 Å^3. Since the reduced unit cell volume is *linearly correlated* with the ratio In:Br in the range of 1:1−1:2 (correlation coefficient = 0.9992), the reduced unit cell volume of the unknown phase, here *ad hoc* assumed to contain *four* reduced formula units, thus corresponds to a composition of approximately $InBr_{1.74} \triangleq In_4Br_{6.96} \approx In_4Br_7$. Supposing a 5% presence of In_4Br_7 within the orange-red precipitate, one would expect the chemical analysis to show an In:Br ratio of about 1:1.04.[38]

Another hint can be drawn from ionic volume increments[39] v_{inc} on the basis of the five well-characterized indium bromides. Approximating $v_{inc}(In^{3+}) \equiv 0$ cm^3/mol, the other ions will have $v_{inc}(In^{2+}) \approx 3.3$ cm^3/mol, $v_{inc}(In^+) \approx 9.2$ cm^3/mol, and $v_{inc}(Br^-) \approx 30.3$ cm^3/mol. Two meaningful ionic compositions for a phase $(2\times)$ In_4Br_7 could be $(In^+)_4(In^{2+})_2(In^{3+})_2(Br^-)_{14}$ or $(In^+)_2(In^{2+})_6(Br^-)_{14}$, thereby reaching molar volumes of 467.6 or 462.4 cm^3/mol for In_8Br_{14}. This value has to be compared with the other hypothetical molar volume of In_8Br_{14} which is 465.3 cm^3/mol, based on the previous cell index proposal.

Most significantly, there is an approximate coincidence between the three strongest reflections reported by Walter et al.[7] for In_4Br_7 (d values of 3.20 Å (strong), 2.97 Å (very strong), and 2.35 Å (moderately strong)) and those of the unknown phase (3.20 Å (medium), 2.99 Å (strong), and 2.35 Å (medium)). In_4Br_7 can be expected to be colorless, probably with a trace of green,[7] and we have indeed found extremely tiny crystals within the orange-red precipitate, almost colorless, with a slight amber-like trace. However, the crystals' quality was too poor to allow for a detailed single crystal study.

(37) There may be attractive interactions between In^+ centers, and a comparison shows these In^+-In^+ distances to be shortest within the bromide (356 pm), slightly longer in the iodide (357 pm) and longest in the (high-temperature) chloride (362 pm); see: Meyer, G.; Staffel, T. *Z. Anorg. Allg. Chem.* **1989**, *574*, 114.

(38) The chemical analysis (In by atomic emission spectroscopy, Br as the weight difference) gives indeed a ratio of 1.03(7) but the standard deviation is too high for a statistically significant conclusion in the above sense.

(39) Biltz, W. *Raumchemie der festen Stoffe*; Verlag von Leopold Voss: Leipzig, Germany, 1934.