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Monocations of bismuth and indium in arene media: A spectroscopic and EXAFS investigation

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The composition of In–$GaCl_3$–benzene and In–$BiCl_3$–$GaCl_3$–benzene solutions was investigated by Raman, UV/Vis, ^{71}Ga and ^{115}In NMR spectroscopy as well as by X-ray absorption fine structure spectroscopy (EXAFS). Indium metal was found to be soluble in $GaCl_3$–benzene solution at room temperature through the reduction of Ga^{III}, producing Ga^+ and In^+ species. The subvalent cations are likely to be stabilized by the interaction with benzene. The use of these solutions as reducing media for $BiCl_3$ leads to the formation of Bi_5^{3+} polycations, with Bi^+ as an intermediate product. No other subvalent bismuth species were detected. Multinuclear NMR experiments show that the reducing agent is Ga^+ rather than In^+. Indium K-edge EXAFS data recorded from solutions without and with subvalent bismuth species present show that In^+ is co-ordinated by benzene (at about 2.9 Å) and chlorine atoms from chlorometalate anions (at about 3.3 Å) in a formal ratio of 1 : 2. Electrospray mass spectroscopic data show that In^+ is most likely co-ordinated by one arene molecule.

Introduction

A spectacular feature of the subvalent chemistry of bismuth is its ability to form homonuclear cluster polycations. The first polycationic bismuth cluster-containing phase was separated from Bi–$BiCl_3$[1] melts and later characterized from single-crystal data as Bi_6Cl_7,[2,3] containing the Bi_9^{5+} polycation. This cluster has since been identified in a number of other compounds (Bi_6Br_7,[4] $Bi_{10}Hf_3Cl_{18}$,[5] $Bi_{10}Zr_3Br_{18}$[6]). Two other types of bismuth polycations were found to exist: Bi_5^{3+} in $Bi_5(AlCl_4)_3$,[7] $Bi_5(GaCl_4)_3$,[8] and Bi_8^{2+} in $Bi_8(AlCl_4)_2$.[3,9] For all these compounds the main synthetic principle remains the same: the oxidation of bismuth metal by its trihalide in molten state in the presence of Lewis acidic metal halides forming stabilizing halogenometalate anions. Only recently, a different synthetic route to the polycations was proposed by the authors of ref. 10. This route, based on the room-temperature oxidation of bismuth metal by $GaCl_3$ in benzene solutions, has led to the formation of Bi_5^{3+} clusters in such solutions. Crystals obtained from these reaction media were found to be the cubic modification of $Bi_5(GaCl_4)_3$,[11] while the crystal structure of the compound of the same composition, previously obtained from molten salt media, was found to be hexagonal.[8] The use of organic solvents also opens up the possibility of a reductive route to subvalent clusters, where the high-valent halide of the cluster-forming element is reduced by a suitable agent other than the corresponding metal. Considering the significantly milder conditions of such syntheses and the opportunities to use reducing agents of various strengths, this "reverse" synthetic route has the potential to produce new cluster species.

It is also important to note that, while the structural chemistry of bismuth polycationic phases has undergone a certain progress since their discovery, very little is known about the reactivity and synthetic chemistry of such species. This may to a large extent be a result of the violent and indiscriminate reactivity of molten salts as reaction media. The synthesis in organic solvent media offers us an opportunity of conducting the reduction and oxidation under very mild conditions, which may prove itself a valuable tool for the studies of bismuth polycations, their structure, stability as well as chemical and physical properties. In this work we report the results of the spectroscopic investigations of subvalent gallium, indium and bismuth species in arene solutions.

Experimental

Chemicals

Commercial Bi (Aldrich, 99.999%), Ga and In metals (both ALFA Chemicals, 99.9999%), anhydrous $GaCl_3$ (ALFA Chemicals, 99.999%), $BiCl_3$ (ALFA Chemicals, 99.999%), $InCl_3$ (ALFA Chemicals, 99.999%), $InBr_3$ (ALFA Chemicals, 99.99%) and InCl (Aldrich, 99.999%) were used as purchased. Anhydrous In_2Cl_4 was prepared from In and $InCl_3$ according to the method decsribed in ref. 12. Benzene (Merck, *p.A.* grade) was distilled and stored over sodium in a glove-box under a dry nitrogen atmosphere.

Sample preparation

Owing to the extremely high moisture sensitivity of the anhydrous metal halides and their solutions used in this work, all operations were performed in a glove-box under dry nitrogen with less than 0.5 ppm water. Standard 5 mm NMR tubes dried under dynamic vacuum at 300 °C were used as sample containers for the NMR and Raman spectroscopic studies. Owing to the sensitivity to light of the $GaCl_3$–benzene solutions, aluminium foil wrappings were used in order to prevent decomposition.

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Spectroscopy

Raman spectra from solutions were recorded using Bruker IFS-66/FRA-106 and Bio-Rad FT-Raman spectrometers equipped with a low power Nd:YAG laser and solid state germanium detector cooled by liquid nitrogen. The resolution used was 4 cm^{-1}. UV/VIS spectra were recorded on a Guided Wave 260 fiber-optics spectrometer designed for the investigation of moisture- and oxygen-sensitive samples.[10] NMR spectra were recorded on a Varian UNITY 300 MHz spectrometer. A 1 M $GaCl_3$ solution in concentrated hydrochloric acid was used as the standard in the ^{71}Ga studies, and a 0.5 M $InCl_3$ solution in concentrated hydrochloric acid as the standard in the ^{115}In studies.

Electrospray mass spectra were obtained in positive and negative ion mode on a VG Platform II mass spectrometer using a mobile phase of dry benzene or toluene. The samples were added to give a mobile phase typically of approximate concentration 0.1 mM. This solution was injected into the spectrometer *via* a Rheodyne injector fitted with a 10 μL sample loop. A Thermo Separation Products Spectra System P1000 LC pump delivered the mobile phase to the mass spectrometer source (at 60 °C) at a flow rate of 0.01 cm^3 min^{-1}, and nitrogen was employed both as a drying and nebulizing gas. Cone voltages were varied from 5 to 150 V in order to investigate the effect of higher voltages on fragmentation of the parent ions. Solvated ions such as $In^+(C_6H_5Me)$ were persistent, although the bare cation In^+ became more conspicuous when the spectra were obtained at higher cone voltages. Theoretical isotope distribution patterns were calculated using the Isotope program[13] and compared with the observed spectra to confirm the identity of each species. The nuclear composition of indium (^{113}In, 4.3%; ^{115}In, 95.7%) provides a distinctive isotopic signature for the In^+ species, with accompanying minor peaks due to the ^{13}C and ^{2}H components of the organic ligand. In the Results and discussion section the mass spectral patterns are identified by the *m*/*z* value of the most abundant peak in the isotopic distribution. Slight hydrolysis caused by the ingress of moisture during sampling was detected by the observation of stray peaks in the negative ion spectrum[14] such as that of $[(GaCl_3)_2OH]^-$ alongside the major anionic signals due to $GaCl_4^-$ and $Ga_2Cl_7^-$.

X-Ray absorption fine structure (EXAFS) studies were performed at the Stanford Synchrotron Radiation Laboratory (SSRL), using beamline 4–1 at 3.0 GeV and 50–60 mA. Monochromatic radiation was obtained from an Si(220) double-crystal monochromator. High-order harmonics were rejected by 50% detuning. Incident and transmitted X-rays were monitored with argon-filled ion chambers. Five to seven scans were made for each sample up to a *k* value of 13 Å^{-1}, internally referenced to the K edge of an indium metal foil to 27.940 keV. The liquid samples were contained in a cell of 1 mm thickness with Kapton film as windows and kept at ambient temperature (about 25 °C). Both transmission and fluorescence (Lytle detector filled with krypton gas) data were recorded. The data were processed by standard procedures for pre-edge subtraction, spline fit and removal.[15] The FEFF 7 program was used to calculate the In–C and In–Cl phase shift and amplitude functions, which were used in the non-linear, least-squares fit of the new EXAFS data.[16,17]

Results and discussion

Indium halides in benzene solution

In the literature, the solubility of indium halides in non-polar organic solvents is generally described as low.[18,19] The initial studies involved an estimation of the solubility of various indium halides in benzene. $InCl_3$–, In_2Cl_4–, InCl– and $InBr_3$–benzene samples with formal molar contents of indium halides varying from 1 to 20 mole% were prepared. However, after equilibration for several days under ambient conditions all the samples were observed still to contain some undissolved halide. Raman data recorded from the samples showed that none of the indium halides investigated is soluble enough to feature in the spectra, suggesting that the solubilities are significantly lower than 10 mM. We can therefore state that no indium halide posesses enough solubility to affect the stability of subvalent bismuth species in benzene media.

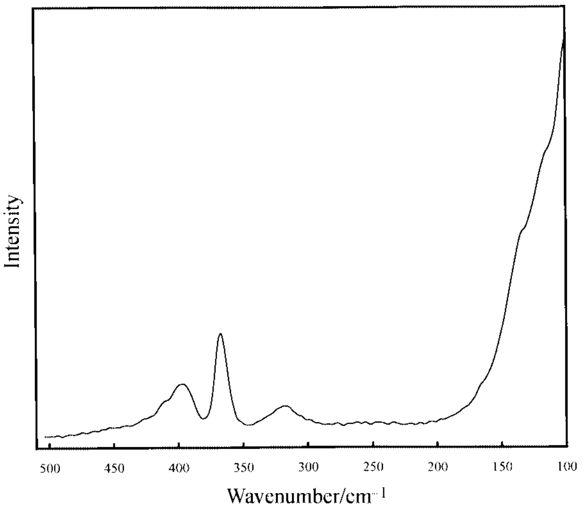


Fig. 1 Raman spectrum of a In–$GaCl_3$–benzene solution.

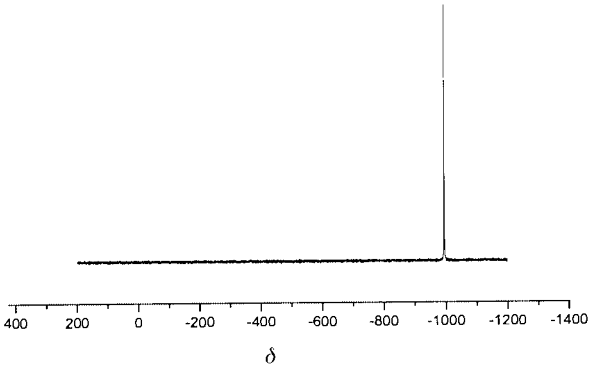


Fig. 2 ^{71}Ga NMR spectrum of a In–$GaCl_3$–benzene solution.

Indium–gallium trichloride–benzene solutions

During the studies described in the previous section it was observed that pieces of indium metal can be dissolved in $GaCl_3$–benzene solutions at room temperature. The process of dissolution is rather slow; it takes about 30 hours to dissolve a batch of several small pieces of metal in a 30 mole% solution of $GaCl_3$ in benzene (the solution of such concentration proved to be close to the optimum from the points of both reasonable dissolution time and distinct spectral features, and hence hereafter is called "standard"). Raman spectra obtained from such solutions display the formation of chlorogallates of general formula $Ga_nCl_{3n+1}^-$ (bands at 364, 396 and 415 cm^{-1} correspond to $n = 2$, and at 317, 364 and 399 cm^{-1} to $n = 3$; Fig. 1), which implies the likely formation of monovalent gallium or indium cations.[20,21]

^{71}Ga NMR spectroscopic studies of these solutions show a sharp peak at δ −998 (Fig. 2), which previously was shown to arise from Ga^I.[10] ^{115}In NMR spectra display a sharp peak at δ −1350 (Fig. 3). On the basis of analogy between the chemistry of Ga and In metal, as well as ^{71}Ga and ^{115}In NMR properties, we assign the sharp peak at high field in the ^{115}In NMR spectra to In^I. Quantitative NMR spectroscopic experiments using the standard-addition technique for four consecutive additions of In metal, where the integral sizes of

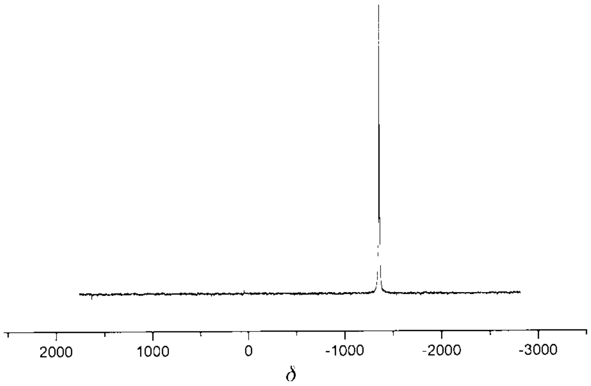


Fig. 3 ^{115}In NMR spectrum of a In–$GaCl_3$–benzene solution.

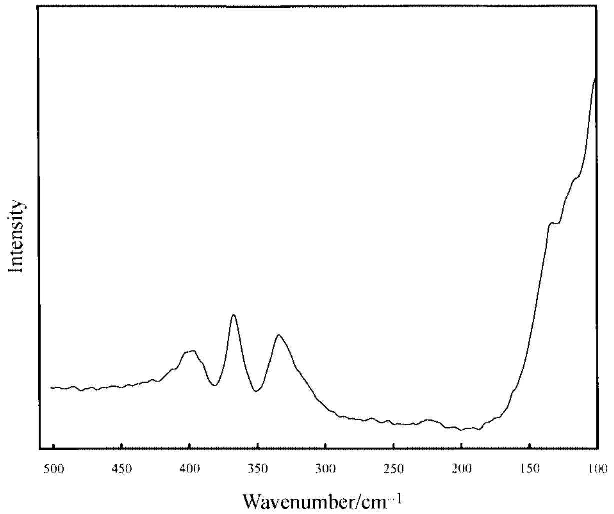


Fig. 4 Raman spectrum of a red In–$BiCl_3$–$GaCl_3$–benzene solution.

gallium(I) and indium(I) peaks were measured after the dissolution of each portion, gave an In : Ga ratio of close to 2 : 1. This corresponds to the following scheme of reaction in solution: $Ga^{3+} + 2\ In^0 \longrightarrow Ga^+ + 2\ In^+$. Another possibility, which would be consistent with the observed In : Ga ratio, is the formation of In_2^{2+} dimeric units. However, the presence of this species is unlikely on the basis of our experimental evidence, namely the lack of an appropriate low-frequency Raman band, the failure to detect any cationic In_2 species in the mass spectra, and the absence of back-scattering effects due to In–In correlations in the EXAFS data (see below) of the In–$GaCl_3$–benzene solutions. Therefore, In^+ is the most probable form of low-valent indium in these solutions, most likely stabilized by the interaction with benzene.

Indium–bismuth trichloride–gallium trichloride–benzene solutions

These solutions, in which Ga^+ and In^+ ions have been generated, might conceivably act as reducing media for $BiCl_3$, with the prospect of making subvalent bismuth species. Such experiments were performed using both crystalline $BiCl_3$ and its solution in 30 mole% $GaCl_3$–benzene solutions. The $BiCl_3$ concentrations used ranged from 10 to 30 mole% with respect to $GaCl_3$. The addition of either several milligrams of crystalline $BiCl_3$ or several drops of its $GaCl_3$–benzene solution to the previously described "standard" In–$GaCl_3$–benzene solution at room temperature leads to an immediate change from faint yellow to green and eventually dark red. Raman spectra of the red solution (Fig. 4) show the appearance of the peak at 135 cm^{-1} assigned to the Bi_5^{3+} polycation.[10] The exact time of the change from green to red heavily depends on the amount of $BiCl_3$ introduced into the sample, normally not exceeding minutes. The use of very dilute $BiCl_3$–$GaCl_3$–benzene solutions (less than 1 mole% $BiCl_3$ with respect to $GaCl_3$), added in a quantity of a few drops to the "standard" In–$GaCl_3$–benzene sample, prolongs the lifetime of the green solutions to several hours. Separate Raman spectral investigations of the green solution proved to be hampered by the high fluorescence humps of the former (green samples sometimes have electronic absorption tails reaching into the NIR region of the YAG laser).

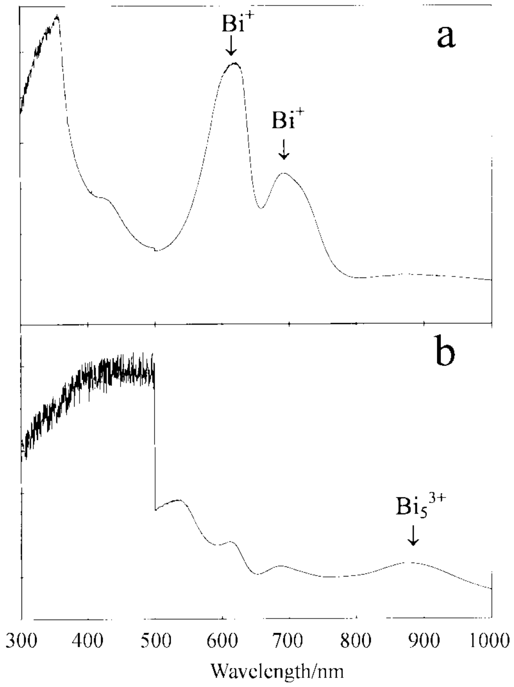


Fig. 5 UV/vis spectrum of (a) a green In–$BiCl_3$–$GaCl_3$–benzene solution, (b) a red In–$BiCl_3$–$GaCl_3$–benzene solution.

UV/Vis spectra obtained within minutes from freshly prepared green solution show peaks at 620 and 700 nm (Fig. 5a), which were assigned to the Bi^+ cation.[22] It should be noted that the green colour must be associated with a Bi-containing species, since the same colour can be obtained by the direct reduction of $BiCl_3$ using Ga–$GaCl_3$–benzene or Sn–$GaCl_3$–benzene solutions as well.[10] As the green-to-red transformation proceeds the intensity of the two Bi^+ peaks gradually decreases, while new peaks at 430 and 880 nm (assigned by the same authors to Bi_5^{3+}) appear and increase in intensity (Fig. 5b).

In order to gain more insight into the state and co-ordination of indium in these solutions, indium K-edge EXAFS data were recorded. The following samples were investigated, (a) In–$GaCl_3$–benzene solution (30 mole% $GaCl_3$ with respect to benzene, 5 mole% In with respect to $GaCl_3$), (b) freshly prepared green In–$BiCl_3$–$GaCl_3$–benzene solution (30 mole% $GaCl_3$ with respect to benzene, 5 mole% In with respect to $GaCl_3$, 5 mole% $BiCl_3$ with respect to $GaCl_3$), (c) the same solution after it had changed to intense red. All three solutions produce quite similar scattering which were analysed from both transmission and fluorescence data. Fourier transformation of the data displays two main peaks of similar magnitude (Fig. 6a). The data analysis shows that both In–Cl and In–C interactions are required in order to obtain a reasonable fit between model and experimental data. For a good coherence in phase, amplitude and envelope to be achieved, the In–Cl correlations must be assumed to be of low co-ordination number and at distances >3 Å. Consequently, the In–C correlations constitute the larger contribution to the data at low *k* values, ending up at distances slightly below 3 Å. The strong damping of the scattering with increasing *k* is indicative of a weak interaction at fairly long distances (about 3 Å or longer; Fig. 6b), *i.e.* a rather poorly defined co-ordination of In^+ often observed for fairly large and monovalent cations (*e.g.* Ag^+ or Tl^+). In order

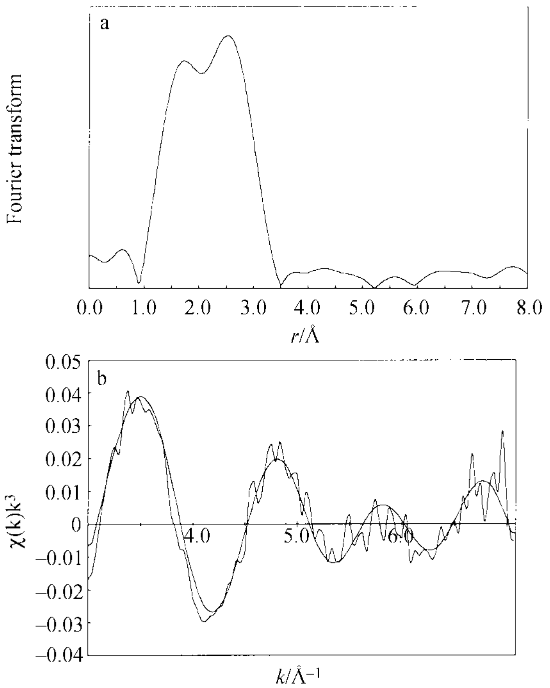


Fig. 6 (a) Fourier transformed radial distribution function of a In–$GaCl_3$–benzene solution. (b) Scattering path with structural model for this solution.

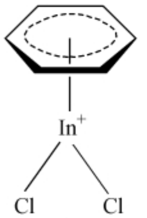
to test different structure models, the interactions with carbon atoms from benzene and chlorine atoms from chlorogallate and chlorobismuthate anions have been considered, in analogy with similar structures known from solid compounds.[23]

The EXAFS data are consistent with a 2 : 1 relation between chloride and η^6-co-ordinated benzene in the closest neighbourhood of In^+. However, the data are not of high enough quality, because of the weak co-ordination of In^+ in the chlorogallate–benzene media, to allow the determination of the absolute number of chlorides (from chlorometalates) and benzene molecules in the co-ordination shell.

Additional information about the weak co-ordination of the aromatic donor molecule to In^+ can be extracted from electrospray mass spectroscopic experiments. The positive ion mass spectrum of an In–$GaCl_3$–benzene sample using toluene as carrier solvent displays a strong signal at *m*/*z* 207 with the isotopic composition predicted for $In^+(C_6H_5Me)$, toluene being in large excess to benzene after dilution from 0.1 M to 0.1 mM. At a cone voltage of 20 V this is the only detectable cationic species of In or Ga. When the potential is raised to 50 V a partial loss of solvent occurs and the spectrum now also shows a peak due to In^+ at *m*/*z* 115 (with its isotopic neighbour at 113). The spectrum at a still higher cone voltage of 150 V recorded an increase in the amount of In^+, relative to $In^+(C_6H_5Me)$, and also contained a significant peak at *m*/*z* 161/163 which signals the presence of $Ga^+(C_6H_5Me)$. Although this species is expected to be present on chemical grounds, being formed during the preparation by the reduction of Ga^{III} by indium, its signal only appears when a high cone voltage is used. Hence, there is a possibility that Ga^+ species are being regenerated during the ionization process. Ions that are observed at low cone voltage (typically 20–40 V) can confidently be assumed to be pre-existing species in the solution. This is the case for $In^+(C_6H_5Me)$.[24,25]

In order to investigate further the solvation of In^+, a small quantity of 1,3,5-trimethylbenzene (mesitylene) was added to a toluene solution of the In–$GaCl_3$–benzene sample and mass spectroscopic data were collected at various cone voltages. These spectra had lost the peak at *m*/*z* 207 due to $In^+(C_6H_5Me)$ but contained that of $In^+(C_6H_5Me_3)$ at *m*/*z* 277 in its place, showing that the toluene molecule had been replaced by mesitylene, being a more effective soft donor. Hence, the electrospray mass spectroscopic results provide firm support for the existence in solution of species of the type $In^+(Ar)$, where Ar represents a single molecule of an aromatic donor. However, no evidence was obtained for $In^+(Ar)_2$ or other solvated indium(I) species.

A structural model based on the present EXAFS and ESMS evidence has the In^+ ion capped by a single aromatic solvent molecule and also in weak association with two chlorine atoms from the gallates, **1**. This structural model is consistent with the one found for a Ga_3Cl_7–benzene solution.[20] A least-squares fit for the *k* range 2.9–7.4 Å^{-1} is consistent with an In–C(benzene) distance of about 2.96(1) Å and an In–Cl(chlorometalate) distance of about 3.36(3) Å for both the green and red In–$BiCl_3$–$GaCl_3$–benzene solutions. Analogous results were obtained for the Bi-free solution of In–$GaCl_3$–benzene, however the distances are somewhat shorter, 2.86(1) and 3.20(1) Å, respectively. The difference, if real, may reflect differences in co-ordination between In^+ and chloro-bismuthates and -gallates. It should at this point be emphasized that no sign of any heavy backscattering from potential In–In or In–Bi interactions was registered.



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Although the formation of the Bi_5^{3+} polycation clearly demonstrates the possibility to use Ga^I- and In^I-containing solutions for the synthesis of subvalent bismuth species, it does not show which of the two monovalent metal ions is responsible for the reduction of $BiCl_3$. In order to clarify this another NMR spectroscopic experiment was performed. On addition of several portions of crystalline $BiCl_3$ to the "standard" In–$GaCl_3$–benzene solution the intensity of the gallium(I) signal is found to decrease, while the indium(I) signal remains constant. The addition of an excess of bismuth trichloride to the saturated solution causes the gallium(I) signal completely to disappear. However, the intensity of the indium(I) signal is not affected. Thus, we can conclude that it is Ga^I that acts as reducing agent for $BiCl_3$, while indium remains in the solution in the form of monovalent cations.

In conclusion, we can establish In–$GaCl_3$–benzene solutions, containing monovalent indium and gallium cations, as reaction media for the synthesis of subvalent bismuth cations through the reduction of bismuth trichloride. The process of reduction leads to Bi_5^{3+} polycations in solution as the final product, with the formation of Bi^+ cations as an intermediate. The Bi_5^{3+} cation can be isolated in the compound $Bi_5(GaCl_4)_3$.[10,11] No data indicative of the presence of other subvalent bismuth species were obtained. The In^+ cation was shown to resist the oxidizing effect of $BiCl_3$ at room temperature, which means that no chloroindate anions are formed in such solutions. Hence, the prospect of obtaining crystals containing bismuth polycations stabilized by chloroindate anions is unlikely in contrast to the proven effect of chlorogallate anions.

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