# Improvements of and Insights into the Isolation of Bismuth Polycations from Benzene Solution – Single-Crystal Structure Determinations of $Bi_8[GaCl_4]_2$ and $Bi_5[GaCl_4]_3$

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The synthesis, crystal growth and structure are reported for the two salts $Bi_5[GaCl_4]_3$ and $Bi_8[GaCl_4]_2$. The compounds are prepared from a solution of $BiCl_3$ and $GaCl_3$ in benzene, using gallium metal as reducing agent. $Bi_8[GaCl_4]_2$ contains a $Bi_8^{2+}$ polycation that, essentially, adopts an ideal square antiprismatic geometry. The compound crystallizes in the $P6_3$ space group; $a = 17.760(2)$ Å and $c = 12.979(3)$ Å. $Bi_5[GaCl_4]_3$ crystallizes in the $R3c$ space group, $a = 11.814(2)$ Å, $c = 29.974(3)$ Å, and contains a $Bi_5^{3+}$ cation adopting a trigonal-bipyramidal geometry. The cation is slightly distorted from the ideal $D_{3h}$ symmetry.

## Introduction

Main group clusters constitute an odd group of molecular and ionic species that have long intrigued chemists. Within this group, bismuth polycations have been one of the most studied families of species, primarily because several subvalent cations have been observed, e.g. $Bi^+$, $Bi_5^{3+}$, $Bi_8^{2+}$ and $Bi_9^{5+}$.[1,2]

There are several synthetic schemes practicable for producing bismuth polycations. In early studies, syntheses were performed at high temperature by dissolving bismuth metal in liquid $BiX_3$ and/or $AlX_3$ (X = Cl, Br, I).[3–9] In these systems, several polycations were identified in solid state or in solution, mainly using X-ray diffraction and spectroscopy. In particular, both $Bi_5^{3+}$ and $Bi_8^{2+}$ are observed when Bi metal is dissolved in liquid $BiCl_3$–$3AlCl_3$. The major product is controlled by the acidity of the system, which, in turn, is controlled by an excess of $AlCl_3$. Due to slow equilibration, supercooling phenomena and problems with twinning, no single crystals were obtained containing either $Bi_5^{3+}$ or $Bi_8^{2+}$ in these early investigations. Therefore, this route was later reconsidered and refined with the purpose of obtaining single crystals of high quality, which allowed better characterization of the two salts $Bi_5[AlCl_4]_3$ and $Bi_8[AlCl_4]_2$.[10–12] Recently, this type of route has again been utilized in the synthesis of $Bi_8[InBr_4]_2$ [13] and $Bi_8[Ta_2O_2Br_7]_2$.[14]

A second synthetic route to subvalent bismuth cations was later proposed, when evidence for the formation of $Bi_5^{3+}$ and $Bi_8^{2+}$ in superacidic media was found.[15] For such media, the products contain, predominantly, $Bi_5^{3+}$, while $Bi_8^{2+}$ could be observed as an intermediate.

A decade ago, a third method suitable for the production of bismuth polycations was presented; on adding bismuth metal to a $GaCl_3$–benzene solution, spectroscopic evidence of a dissolved subvalent bismuth species, $Bi_5^{3+}$, was obtained.[16] This was later supplemented by the isolation of a cubic modification of $Bi_5[GaCl_4]_3$, as a powder, by mixing the Bi–$GaCl_3$–benzene solution with *n*-heptane.[17] The advantage of this route is that it is conducted at room temperature using standard chemicals, while still being reasonably quick. However, only one bismuth polycation has been isolated, and it has been possible to crystallize the solid compound only as powder and not as single crystals. To improve the applicability of this synthetic route, methods for obtaining large single crystals have to be devised. Furthermore, as different bismuth polycations have been isolated from very similar conditions using solid-state techniques, small modifications in the conditions could also generate polycations other than $Bi_5^{3+}$ when using arene reaction media. This hypothesis is additionally supported by quantum chemistry calculations that show several small bismuth clusters, so far not isolated experimentally, to be electronically stable.[18]

We report here a successful method for obtaining high-quality single crystals of subvalent bismuth species in benzene solution. This procedure has been used to isolate a new compound, $Bi_8[GaCl_4]_2$, for which the structure is reported. A re-determination of the structure of trigonal $Bi_5[GaCl_4]_3$ is also reported, together with a discussion on the existence and nature of the cubic modification of $Bi_5[GaCl_4]_3$.

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## Results and Discussion

### Synthesis and Crystal Growth

The original procedure for the synthesis of $Bi_5^{3+}$ in $GaCl_3$–benzene solution used bismuth metal as starting material, which was to be oxidized by $GaCl_3$ to subvalent bismuth species. However, an alternative route is feasible using $GaCl_3$–benzene solution; instead of oxidizing bismuth metal, $BiCl_3$ can be reduced to subvalent species by Ga[$GaCl_4$], mimicking the reaction of Ga–$GaCl_3$–$BiCl_3$ in melts.[19] In this work, the primary procedure has been the reductive route, i.e. the reduction of $BiCl_3$ using Ga[$GaCl_4$]. This alternative is faster and also allows control of bismuth concentration.

As mentioned above, $Bi_5[GaCl_4]_3$ can be precipitated from the prepared benzene solution by shaking this solution with an alkane (e.g. *n*-heptane), producing a red powder.

If larger crystals are desired, a lower rate of mixing with the alkane, e.g. by applying diffusion techniques, could be effective. However, with a Bi–$GaCl_3$–benzene solution, the use of slow diffusion with an alkane normally ends in the solidification of a deeply red, glass-like phase at the bottom of the reaction vessel, together with some red powder. Nevertheless, in rare cases, brown, crystal-like cubes have been obtained using this method. The unit cell has been found to be *F*-centered cubic with a cell parameter of 17.1 Å. This corresponds well to the parameters of the cubic modification of $Bi_5[GaCl_4]_3$, which has previously been reported as the product of this reaction.[17] However, as with the powder data, only low-angle reflections are detected in X-ray diffraction experiments on the single crystals, indicating a disordered structure. The nature of this phase, and its relation to trigonal $Bi_5[GaCl_4]_3$, which has been more satisfactorily characterized, will be further discussed below.

Thus, the use of solely aliphatic hydrocarbons to obtain large single crystals from a $Bi_n^{x+}$–$GaCl_3$–benzene solution has clearly proved to be at best very unreliable. This is due to the extremely small solubility of the subvalent bismuth species in non-aromatic solvents. For quicker and more reproducible results, other ways have to be explored.

In this case, the obvious choice is to try aromatic hydrocarbons similar to benzene but exhibiting a lower solubility of $GaCl_3$ and $Bi_n^{x+}$, thus creating a less dramatic decrease in solubility using diffusion techniques. In this particular work, mesitylene has been used for this purpose.

If mesitylene is added on top of a *saturated* $Bi_n^{x+}$–$GaCl_3$–benzene solution, single crystals are formed, within a couple of days, in the upper part of the benzene phase. Saturation of the benzene solution is important because of the moderately high solubility of the polycations in mesitylene; otherwise only dilution, and no crystallization, will occur. The benzene phase is saturated by an initial extraction (referring mainly to excess $GaCl_3$) using *n*-heptane, but carefully avoiding the precipitation of cubic $Bi_5[GaCl_4]_3$.

Using this procedure, two different types of crystals can be isolated, i.e. black cylinders and red square plates. The black cylinder-shaped crystals consist of $Bi_8[GaCl_4]_2$, a previously uncharacterized compound. The crystals are of varying sizes, the largest being around 0.5 mm.

The red crystals, however, are often very small, <0.1 mm, and tend to form aggregates, making it difficult to select a suitable single crystal for crystallographic investigation. Even so, it has been possible to establish these crystals as trigonal $Bi_5[GaCl_4]_3$, which has previously been synthesized by a solid state route. This structure has so far only been characterized using powder data.[20]

Hence, as for the solid-state and superacid-based methods mentioned above, it can be observed that there is a special relationship between the two cations $Bi_5^{3+}$ and $Bi_8^{2+}$, and different cations may appear in systems having only slightly different conditions. This is not very controversial, merely reinforcing the proposition that the $GaCl_3$–benzene system can be regarded as a “pseudo-melt”.[21]

Of the two cations, $Bi_5^{3+}$ is obviously the most stable in solution; no traceable amounts of $Bi_8^{2+}$ were discovered using UV/Vis spectroscopy in earlier studies on this system. Likewise, only $Bi_5[GaCl_4]_3$ is formed when precipitating using an alkane. However, in contrast, the more abundant product from the approach reported above is $Bi_8[GaCl_4]_2$, while synthetic efforts aimed to generate $Bi_5[GaCl_4]_3$ exclusively in most cases have failed. Instead, red crystals of this compound are most frequently found when the two crystal types are formed in the same experiment. Again, this indicates the very subtle shifts in concentration, of one or more of the reactants, needed to render different solid products. In particular, $Bi_5[GaCl_4]_3$ displays a very narrow window of concentration in which single crystals will be formed. Exactly how this equilibrium is controlled and the mechanism for the formation and crystal growth of $Bi_8[GaCl_4]_2$ from a solution dominated by $Bi_5^{3+}$ are questions for future research. Furthermore, it is puzzling that only these two polycations are formed as calculations have shown that several other bismuth polycations should be isolable.[18]

The route described in this work offers a very easy and good alternative way of producing high-quality crystals containing the $Bi_8^{2+}$ polycation. The crystals can be obtained at room temperature after only a couple days of treatment. However, findings of $Bi_5[GaCl_4]_3$ crystals are far sparser, demonstrating that the optimal conditions for their isolation have very narrow borders, which need to be clarified in order for the described route to this compound to be reliable. The general usefulness of the above method has already been proven with the successful synthesis and crystal growth of $Sb_8[GaCl_4]_2$ – the first structural characterization of an antimony polycation.[22]

### Crystal Structure of $Bi_8[GaCl_4]_2$

Table 1 gives the atomic parameters for this compound. The structure consists of $Bi_8^{2+}$ polycations and tetrahedral $GaCl_4^-$ anions (Figure 1). The $Bi_8^{2+}$ polycation geometry is very close to an ideal square antiprism ($D_{4d}$ symmetry), although its crystallographic symmetry is only $C_1$. The structure is very similar to that reported earlier for $Bi_8[AlCl_4]_2$.[10,12] However, the space group chosen for the current chlorogallate structure is $P6_3$ while the aluminate structure was refined in space group $P6_3/m$. In the current structure the anions are all aligned and ordered, in contrast to $Bi_8[AlCl_4]_2$ in which they are reported to be disordered. Notably, all $GaCl_4$ tetrahedra on the $c$ axis possess one corner pointing into the positive $c$ direction (Figure 2). Adding a mirror plane perpendicular to $c$ to this structure would necessarily cause disorder of the anions, leaving the cations essentially unchanged because the latter need only a minor distortion to accommodate such a mirror plane. The choice of space group $P6_3$ therefore appears unambiguous, leaving open the question of whether the chloroaluminate and chlorogallate really adopt slightly different structures or if a redetermination of the chloroaluminate in space group $P6_3$ might lead to an improved structure model without anion disorder.

Table 1. Final coordinates and isotropic thermal parameters for $Bi_8[GaCl_4]_2$

| Atom | $x/a$ | $y/b$ | $z/c$ | $B$ [Å$^2$] |
|---|---|---|---|---|
| Bi(1) | 0.8561(1) | 0.6287(2) | 1.1523(1) | 3.7(1) |
| Bi(2) | 0.9608(2) | 0.5324(1) | 1.1440(1) | 4.4(1) |
| Bi(3) | 0.9597(2) | 0.5390(1) | 0.9036(1) | 3.9(1) |
| Bi(4) | 0.8545(1) | 0.6332(2) | 0.9158(1) | 4.4(1) |
| Bi(5) | 1.1278(1) | 0.6627(1) | 1.0256(2) | 4.6(1) |
| Bi(6) | 1.0530(2) | 0.7358(2) | 0.8655(2) | 3.9(1) |
| Bi(7) | 0.9781(1) | 0.8001(1) | 1.0387(2) | 4.9(1) |
| Bi(8) | 1.0545(2) | 0.7282(2) | 1.1971(2) | 4.1(1) |
| Ga(1) | 2/3 | 1/3 | 0.7336(5) | 2.5(1) |
| Ga(2) | 1/3 | 2/3 | 0.6983(6) | 3.3(2) |
| Ga(3) | 1 | 1 | 0.7915(8) | 2.9(1) |
| Ga(4) | 0.6388(3) | 0.6944(2) | 1.0079(3) | 3.4(1) |
| Cl(1) | 2/3 | 1/3 | 0.567(1) | 4.6(4) |
| Cl(2) | 0.7848(9) | 0.340(1) | 0.789(1) | 4.3(4) |
| Cl(3) | 1/3 | 2/3 | 0.538(3) | 14.5(8) |
| Cl(4) | 0.4455(9) | 0.784(1) | 0.756(1) | 5.2(4) |
| Cl(5) | 1.1021(8) | 0.9793(9) | 1.236(1) | 6.5(4) |
| Cl(6) | 1 | 1 | 0.959(1) | 3.9(4) |
| Cl(7) | 0.883(1) | 0.594(1) | 0.653(1) | 9.2(6) |
| Cl(8) | 0.7632(8) | 0.8013(8) | 0.967(1) | 6.8(4) |
| Cl(9) | 0.6544(6) | 0.5802(6) | 1.015(2) | 5.3(4) |
| Cl(10) | 0.8668(8) | 0.5436(7) | 1.3995(9) | 4.0(3) |

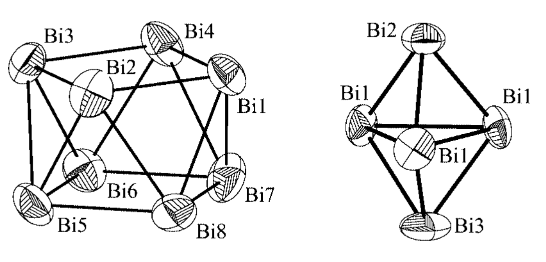

Figure 1. Polycations $Bi_8{}^{2+}$ in $Bi_8[GaCl_4]_2$ (left) and $Bi_5{}^{3+}$ in $Bi_5[GaCl_4]_3$ (right); thermal ellipsoids drawn at a 70% probability level

As expected, the Bi–Bi distances of the polycation are very similar to those of the previously reported structure; the bond lengths vary in the range 3.07–3.12 Å (Table 2). The average bond length within the square faces is 3.09 Å and the average bond length between the two squares is 3.10 Å (3.09 and 3.11 Å, respectively, in $Bi_8[AlCl_4]_2$). Quantum chemical calculations have previously suggested that the bonding within the square faces are more localized relative to the bonding between the squares.[18] However, in the optimized theoretical structure, the difference between the inter- and intra-square distances is larger than in the experimentally found polycations; the inter/intra distance ratio is 1.025 theoretically and 1.004 in the structure presented here. This deviation in bond length ratio may indicate that the bonding of the polycation is more extensively delocalized than the calculations predict. The Ga–Cl distances in the anions show a small variation, 2.08–2.18 Å, with the exception of one distance of 2.01 Å. The shortest Bi–Cl distance is 3.44 Å, indicating that the cation–anion interactions are weak.

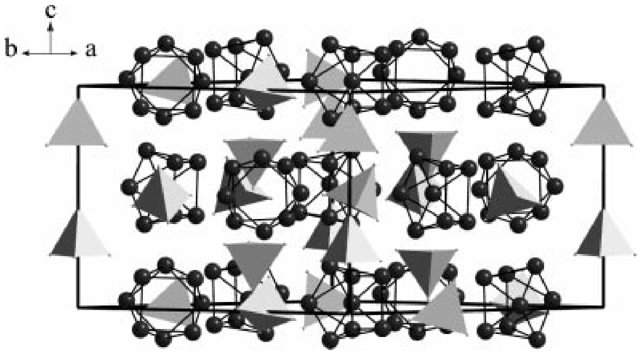

Figure 2. Unit cell of $Bi_8[GaCl_4]_2$ in a view along [110]; $GaCl_4^-$ entities on the $c$ axis are aligned, thus excluding the possibility of a mirror plane perpendicular to this axis

### Crystal Structure of $Bi_5[GaCl_4]_3$

The structure consists of the well-known $Bi_5{}^{3+}$ polycation and $GaCl_4^-$ anions. Atomic parameters are presented in

Table 2. Comparison of unit cell parameters [Å] and distances [Å] in $Bi_8[GaCl_4]_2$ and $Bi_8[AlCl_4]_2$; atom labels given in Figure 1

| Parameter | $Bi_8[GaCl_4]_2$ | $Bi_8[AlCl_4]_2$[12] |
|---|---|---|
| Space group | $P6_3$ | $P6_3/m$ |
| $a$ [Å] | 17.760(2) | 17.854(4) |
| $c$ [Å] | 12.979(3) | 12.953(3) |
| Bi(1)–Bi(2) | 3.095(3) | 3.086(6) |
| Bi(2)–Bi(3) | 3.123(2) | 3.098(6) |
| Bi(3)–Bi(4) | 3.072(3) | 3.086(6) |
| Bi(1)–Bi(4) | 3.071(2) | 3.078(6) |
| Bi(5)–Bi(6) | 3.079(3) | 3.086(7) |
| Bi(6)–Bi(7) | 3.107(3) | 3.085(6) |
| Bi(7)–Bi(8) | 3.072(3) | 3.085(6) |
| Bi(5)–Bi(8) | 3.084(3) | 3.086(7) |
| Bi(1)–Bi(7) | 3.089(3) | 3.122(5) |
| Bi(1)–Bi(8) | 3.107(3) | 3.123(4) |
| Bi(2)–Bi(5) | 3.106(3) | 3.104(5) |
| Bi(2)–Bi(8) | 3.091(3) | 3.092(5) |
| Bi(3)–Bi(5) | 3.112(3) | 3.104(5) |
| Bi(3)–Bi(6) | 3.067(3) | 3.092(5) |
| Bi(4)–Bi(6) | 3.124(3) | 3.123(5) |
| Bi(4)–Bi(7) | 3.105(3) | 3.122(5) |

Table 3 and the unit cell is displayed in Figure 3. $Bi_5^{3+}$ is almost a perfect trigonal bipyramid (Figure 1). This compound has previously been characterized from powder data[20] and, furthermore, it exists in an analogous aluminate structure, $Bi_5[AlCl_4]_3$.[6,11] However, the space group of the structure in the present work was found to be $R3c$, while the earlier studies found it to be $R\bar{3}c$. Even in this study on $Bi_5[GaCl_4]_3$, a structural model could be obtained in space group $R\bar{3}c$. The final result of the structure refinement yielded a much poorer result, though, with significantly larger $R$ factors and difference-Fourier peaks in the range –5 to 5 e Å$^{-3}$ in the proximity of the Bi cation. Additionally, the geometry of the cation changed significantly when the structure was refined in $R3c$. The apical bismuth atoms, which were crystallographically equivalent in $R\bar{3}c$, were refined to rather different final positions in space group $R3c$. This yields a cluster cation with two significantly different bond lengths between the equatorial atoms and the two apical ones, i.e. 2.97 and 3.02 Å, respectively.

Table 3. Final coordinates and isotropic thermal parameters for trigonal $Bi_5[GaCl_4]_3$

| Atom | *x*/*a* | *y*/*b* | *z*/*c* | *B* [Å$^2$] |
|---|---|---|---|---|
| Bi(1) | 0.0038(3) | 0.1635(2) | 0.24988(18) | 4.6(1) |
| Bi(2) | 0 | 0 | 0.17179(5) | 4.7(1) |
| Bi(3) | 0 | 0 | 0.32572(5) | 6.3(2) |
| Ga(1) | 0.4782(4) | 0.4795(4) | 0.2506(3) | 2.4(1) |
| Cl(1) | 0.592(1) | 0.581(1) | 0.3078(4) | 2.8(3) |
| Cl(2) | 0.581(1) | 0.585(1) | 0.1908(4) | 4.1(3) |
| Cl(3) | 0.455(1) | 0.283(1) | 0.2430(5) | 3.9(3) |
| Cl(4) | 0.286(1) | 0.451(1) | 0.2603(5) | 4.9(4) |

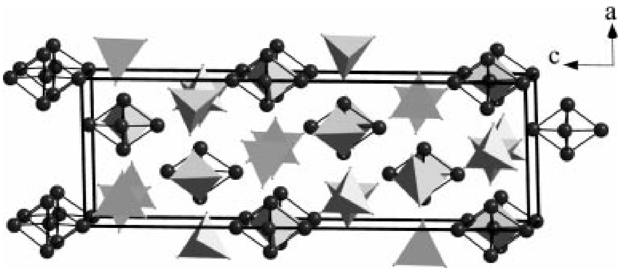

Figure 3. Unit cell of $Bi_5[GaCl_4]_3$ in a view along the *b* axis

To resolve unambiguously the choice of space group in this case, an experimental proof of noncentrosymmetry would be welcome. Unfortunately, so far, such an experiment has proved impossible due to the difficulties in controlling the production of $Bi_5[GaCl_4]_3$ single crystals, as described above. The ultimate choice of the non-centrosymmetric space group is mainly based on the fact that a removal of the centre of symmetry allows a refinement of a structural model that fits the diffraction data considerably better. Table 4 summarizes the bond lengths in $Bi_5[GaCl_4]_3$ and $Bi_5[AlCl_4]_3$.

Table 4. Comparison of unit cell parameters [Å] and distances [Å] in trigonal $Bi_5[GaCl_4]_3$ and $Bi_5[AlCl_4]_3$; atom labels are given in Figure 1

| Parameter | $Bi_5[GaCl_4]_3$ | $Bi_5[AlCl_4]_3$[11] |
|---|---|---|
| Space group | $R3c$ | $R\bar{3}c$ |
| *a* [Å] | 11.814(2) | 11.860(3) |
| *c* [Å] | 29.974(3) | 30.100(8) |
| Bi(1)–Bi(1) | 3.3062(14) | 3.319(2) |
| Bi(1)–Bi(2) | 3.020(4) | 3.007(2) |
| Bi(1)–Bi(3) | 2.968(4) | 3.007(2) |

In the $R3c$ space group the symmetry of the cluster cation is lowered from the theoretically predicted $D_{3h}$, which is predestined with the centric space group, to $C_{3v}$, as described above. A similar small deviation from the ideal geometry has previously been reported for the isoelectronic $Sn_5^{2-}$, while $Pb_5^{2-}$ retained the $D_{3h}$ symmetry.[23]

## Cubic Modification of $Bi_5[GaCl_4]_3$

As mentioned above, brown, cube-shaped crystallites have on rare occasions been obtained from benzene solution using a slow diffusion technique with *n*-heptane. These crystallites have an F-centered cubic unit cell with a cell parameter of 17.1 Å, corresponding well to the previously reported cubic modification of $Bi_5[GaCl_4]_3$.

This biphasic nature of $Bi_5[GaCl_4]_3$ is puzzling – is the cubic form really a separate phase or is it simply a twinned form of the hexagonal modification? Powder diffraction clearly indicates that the two phases are distinct,[17] but if the trigonal form is cast in a rhombohedral setting it yields cell parameters that differ from the cubic form only by 0.1 Å and 1°. Considering the quality of the data from the cubic modification, such a deviation is not unreasonable; the reflection profiles are very broad. Moreover, the atomic positions in the trigonal form nearly match onto those of the solution of the cubic structure, showing that the two are clearly locally very similar. Hence, in some aspects, the cubic form can reasonably be assumed to represent a microtwinned variety of the trigonal form. The slight mismatch of cell parameters is then explained by the strain caused by the clamping of slightly dissimilar dimensions onto each other.

Does this mean that the two forms are really different phases? Probably yes. The extensive broadening of the reflections in the cubic phase and the lack of high-angle reflections imply that the average domain size is very small, i.e. twinning occurs close to the unit cell level. The two forms are expected to have different heats of formation because of this (they clearly have different diffraction patterns) and they will form at slightly different temperatures and/or solvent conditions. However, no transition between the two phases could be found by thermal analysis (differential scanning calorimetry) before the compounds decomposed (disproportionation at ca. 170–190 °C).

## Conclusions

We have presented an easy route to high-quality single crystals containing bismuth polycations that were previously very difficult to obtain, demanding high temperature and long annealing times. By the stratification of mesitylene on top of a polycation-containing benzene solution, single crystals are formed. Two different crystal structures have been isolated; the previously uncharacterized compound $Bi_8[GaCl_4]_2$ and $Bi_5[GaCl_4]_3$, which has previously been characterized using powder diffraction. It is suggested that the space group of both current chlorogallate structures differs somewhat from that of known aluminate compounds.

The formation of large single crystals of $Bi_5[GaCl_4]_3$ appears to demand very special conditions; the abundant product of the approach described here is, therefore, $Bi_8[GaCl_4]_2$. This is somewhat surprising considering that the dominant polycation in benzene solution is clearly $Bi_5^{3+}$.

As to whether a cubic $Bi_5[GaCl_4]_3$ phase really exists, it is suggested that this phase is a likely consequence of microtwinning of the trigonal modification.

## Experimental Section

**General:** $GaCl_3$ (Aldrich, anhydrous, 99.99%), $BiCl_3$ (Alfa, anhydrous, 99.999%) and gallium metal (Alfa, 99.999%) were used as received. Benzene (Fluka, 99.5%), heptane (Merck, 99%) and mesitylene (Janssen, 99%) were dried using molecular sieves. Due to the air and moisture sensitivity of the reactants and products, all synthetic work was performed in a glove-box under nitrogen (<1 pm $H_2O$ and $O_2$).

**Preparation of Bismuth Polycation Solutions:** A standard reductive-route experiment was performed as follows: $BiCl_3$ (0.22 g, 0.70 mmol) was added to $GaCl_3$ (0.66 g, 3.7 mmol) dissolved in benzene (1.0 mL) in a standard NMR tube. A second solution was produced by adding gallium metal (0.080 g, 1.1 mmol) to a solution of $GaCl_3$ (0.66 g, 3.7 mmol) in benzene (1.0 mL). After 24 h, undissolved gallium metal was removed from the latter solution, and the two solutions were mixed and left overnight. The final solution was deep red.

**Isolation of Single Crystals:** The solution was first concentrated by gentle extraction using *n*-heptane (2 mL), carefully avoiding precipitation. The heptane phase was then removed and mesitylene (2 mL) was stratified on top of the red solution. After 24–48 h, after one exchange of the mesitylene phase, crystals had formed on the glass wall of the NMR tube, near the phase border. Most of the crystals were black cylinders, but smaller, plate-shaped, red crystals could also be obtained above the black ones, i.e. closer to the mesitylene phase.

**Thermal Analysis:** Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer DSC 7 instrument. Samples were sealed in aluminium capsules inside the glove box prior to the measurements.

**X-ray Crystallographic Data and Refinement of the Structures:** Table 5 summarizes the crystallographic data for $Bi_8[GaCl_4]_2$ and $Bi_5[GaCl_4]_3$. The crystals were sealed in 0.5 mm Lindemann capillaries under dry nitrogen. Diffraction data were collected with a Bruker-Nonius KappaCCD diffractometer.

Table 5. Unit cell parameters and experimental crystal data of $Bi_8[GaCl_4]_2$ and $Bi_5[GaCl_4]_3$

| Compound | $Bi_8[GaCl_4]_2$ | $Bi_5[GaCl_4]_3$ |
|---|---|---|
| Molecular mass [g mol$^{-1}$] | 2094.88 | 1679.46 |
| Crystal system | hexagonal | trigonal |
| Space group | $P6_3$ (no. 173) | $R3c$ (no. 161) |
| $a$ [Å] | 17.760(2) | 11.814(2) |
| $c$ [Å] | 12.979(3) | 29.974(3) |
| $V$ [Å$^3$] | 3545(1) | 3623.2(9) |
| $Z$ | 6 | 6 |
| $D_{\text{calcd.}}$ [g cm$^{-3}$] | 5.89 | 4.62 |
| Crystal size [mm] | 0.15 × 0.15 × 0.10 | 0.10 × 0.10 × 0.05 |
| Temperature [K] | 293 | 293 |
| Radiation, $\lambda$ [Å] | Mo-$K_\alpha$, 0.71073 | Mo-$K_\alpha$, 0.71073 |
| Monochromator | graphite | graphite |
| Scan range, $2\theta$ [°] | 9.18–55.02 | 9.64–55.00 |
| No. measured reflections | 21249 | 11286 |
| No. unique reflections | 4679 | 1837 |
| No. reflections [$I > 2\sigma(I)$] | 3396 | 1303 |
| No. parameters refined | 173 | 62 |
| Max/min Fourier peak [e Å$^{-3}$] | 1.98/–1.90 | 1.77/–2.25 |
| $R(\lvert F\rvert)$, all | 0.112 | 0.099 |
| $R(\lvert F\rvert)$, $I > 2\sigma(I)$ | 0.070 | 0.060 |
| $wR(F^2)$, all | 0.116 | 0.121 |
| GOF | 1.283 | 1.215 |

**$Bi_8[GaCl_4]_2$:** The compound crystallizes in the hexagonal system, Laue group $6/m$. The systematic absences ($00l$, $l = 2n$) led to the possible space groups $P6_3$ and $P6_3/m$ of which the former, non-centrosymmetric one was confirmed during structure determination. The structure was refined assuming an inversion twin (ratio of the twin components: 0.8:0.2).

**$Bi_5[GaCl_4]_3$:** The compound crystallizes in the rhombohedral system, Laue group $-3m$. Systematic absences led to the possible space groups $R3c$ and $R\bar{3}c$. A structure model could be obtained in space group $R\bar{3}c$. After the refinement, rather large peaks (+5/–5 e Å$^{-3}$) were still present in the difference-Fourier map close to the Bi atoms and on opposite sides of them. The symmetry was therefore lowered to $R3c$. Upon re-refinement of the structure, the geometry of the cation changed slightly, but significantly: Bond lengths in the equatorial plane decreased from 3.284(5) to 3.269(5) Å. The structural change along the $c$ axis is even more significant: The two apical Bi atoms, which were crystallographically related by a two-fold rotation axis in space group $R\bar{3}c$, become independent and the bond lengths between them and the equatorial Bi atoms change [Bi(1)–Bi(3) is 2.977(4) Å and Bi(1)–Bi(2) is 3.037(4) Å]. The difference between these interatomic distances is thus 15σ. Additionally, the maximum and minimum difference-Fourier peaks shrunk to more reasonable levels (1.77/–2.25 e Å$^{-3}$), which makes the description of the structure in space group $R3c$ appear more appropriate.

All atoms were refined using anisotropic temperature parameters. Numerical absorption corrections were applied.[24] All structures were solved and refined using direct methods and difference Fourier techniques using SHELXS97/SHELXL97.[25,26] Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, Fax: +49-7247-808-666; E-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-414089 ($Bi_5[GaCl_4]_3$) and CSD-414090 ($Bi_8[GaCl_4]_2$).

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