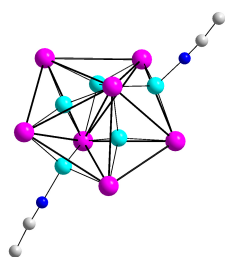
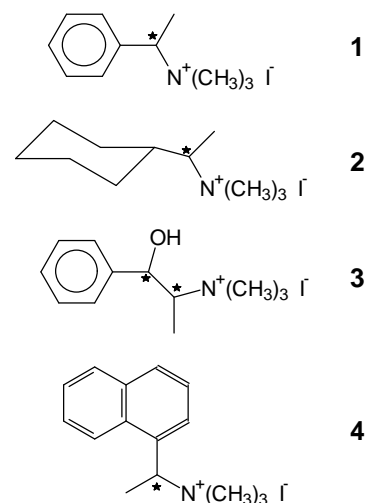
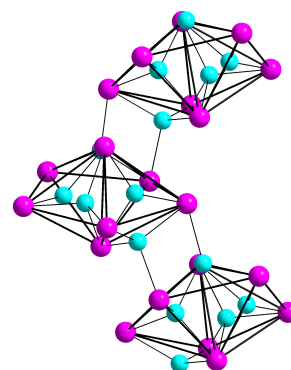


## 8. Abstract

Trying to examine the influence of chirality of cations on the formation of iodocuprate(I) and iodoargentate(I) anions in the reaction of the four chiral cations (1-Phenylethyl)trimethylammoniumiodine **1**, (1-Cyclohexylethyl)trimethylammoniumiodine **2**, (2-Hydroxy-1-methyl-2-phenylethyl)-trimethylammonium-iodine **3** and (1-(1-Naphthyl)ethyl)trimethylammonium-iodine **4** with copperiodine or silveriodine one can find some new, partly chiral iodocuprates(I) and iodoargentates(I). It was possible to determine the structures by X-ray methods.

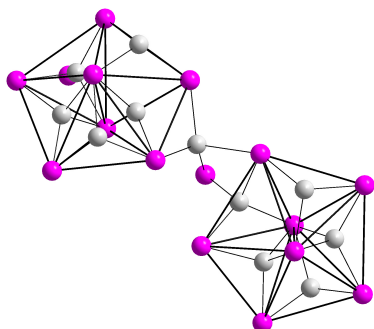


The chiral pentagonal bipyramidal anion  $[\text{Cu}_5\text{I}_7 \cdot 2 \text{CH}_3\text{CN}]^{2-}$  can be found with one enantiomorph of the cation **1**. It was also possible to determine the structure of the chiral anion  ${}^1[\text{Cu}_5\text{I}_7]^{2-}$ , in which pentagonal



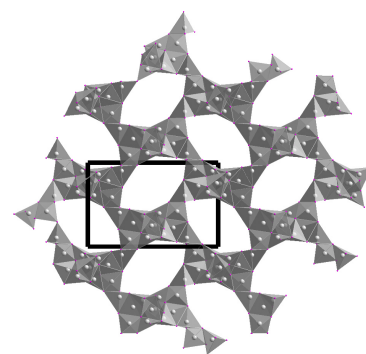
bipyramids form a helical chain. This structure can be interpreted as the polymerization product of the  $[\text{Cu}_5\text{I}_7 \cdot 2\text{CH}_3\text{CN}]^{2-}$  anion by loss of the acetonitril ligands and using iodine of the pentagonal basis of neighbouring bipyramids instead.

The two enantiomorphs of an interesting chiral 3-dimensional structure  $[\text{Ag}_6\text{I}_8]^{2-}$  can be received as products of the reaction of silveriodine with the

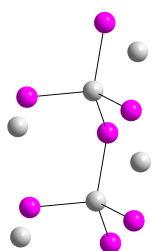


enantiomorphs of the cation **1**. The network is built of pentagonal  $\text{Ag}_5\text{I}_7$  bipyramids connected directly (sharing edges of the pentagonal basis) and using the  $\text{AgI}$ , which takes not part in the formation of the pentagonal bipyramids, containing the cations in the resulting cylindrical cavities. One can suppose properties of a solid

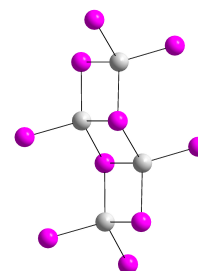
electrolyte considering the structure of these both anions with face-sharing occupied and unoccupied tetrahedrons. An astonishing fact is the crystallization of a totally different anion using the racemic cation **1**. In this case an  $^1_\infty[\text{AgI}_2]^-$  anion (SiS<sub>2</sub>-type) appeared and the same effect using CuI instead of AgI ( $^1_\infty[\text{CuI}_2]^-$  with the racemic cation **1** and chiral  $[\text{Cu}_5\text{I}_7 \cdot 2 \text{CH}_3\text{CN}]^{2-}$  with the enantiomorphs of **1**)



The reactions of the other chiral cations **2**, **3** and **4** with silveriodine only lead to the non-chiral anion  $^1_\infty[\text{Ag}_2\text{I}_3]^-$ , the most common anionic configuration of iodoargentates(I).



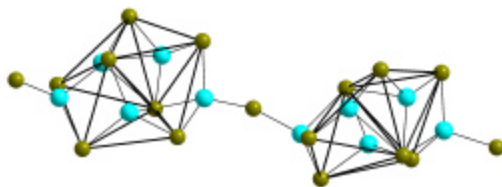
As byproducts of the reaction of AgI with chiral cations two uncommon iodoargentates (I) with solvated  $\text{Ag}^+$  cations can be determined.



Chirality of the cations seems not to be the only factor that influences the formation of iodocuprate(I) and iodoargentate(I) anions. Also the size, the shape and the distribution of the positive charge of the cations have influence on the resulting anions explaining the formation of different structures using similar cations.

The striking problem in this system is the crystallization and the reproduction of the species. The crystal growth is very sensitive to insignificant changes of the reaction conditions and this sensitivity is even higher using chiral substances. We observed this known phenomena especially in the reactions with CuI, where we suppose the existence of the chiral anion  $[\text{Cu}_5\text{I}_7 \cdot 2 \text{CH}_3\text{CN}]^{2-}$  in solution, as opposed to the reactions with AgI (analogous chiral anion  $[\text{Ag}_5\text{I}_7 \cdot 2 \text{CH}_3\text{CN}]^{2-}$  unknown).

Two new Bromocuprates have been prepared and characterized examining the participation of halogenocuprates(I) in the Sandmeyer reaction. Both, one with an isolated  $[\text{Cu}^{\text{II}}\text{Br}_4]^{2-}$  anion and the second with the  ${}^1_{\infty}[\text{Cu}_5\text{Br}_8]^{3-}$  anion, a chain of pentagonal  $\text{Cu}_5\text{Br}_7$



bipyramids connected via the 8<sup>th</sup> Br, represent only intermediate byproducts and not “reactive” intermediates of the Sandmeyer reaction.

As a result of this work one can establish that in the system of halogeno- $d^{10}$ -metallates the “uncommon” anionic configuration of pentagonal bipyramids appears frequently. Iodocuprates(I) with pentagonal bipyramids in their anionic structures have been observed with 5 <sup>[31], [32], [35]</sup>, 4 <sup>[61]</sup>, 3 <sup>[36], [37], [61]</sup> or 2 <sup>[36]</sup> occupied tetrahedral holes. Pentagonal bipyramidal bromocuprates(I) were only known with 5 <sup>[98]</sup> or 3 and iodoargentates(I) only with 2 occupied or completely unoccupied tetrahedral holes <sup>[71]</sup>. The pentagonal bipyramid represents a part of a room-centered icosahedron. This is very similar to a room-centered cuboctahedron, the characteristic of a cubic closest package of spherical particles of the same size. This close or nearly closest package of the halogene atoms with the metal atoms in the tetrahedral holes seems to be the motive power to build the pentagonal bipyramidal configuration in the halogeno- $d^{10}$ -metallate anions.