

V. SUMMARY

The pentahalides of the 5th main group show an interesting structural trend.

PCl_5 is known since 200 years and has a ionic structure in the solid state $[\text{PCl}_4^+][\text{PCl}_6^-]$.

Antimony pentachloride exists in two modifications. It has a trigonal bipyramidal structure and changes below -55°C reversibly into a double chlorine bridged dimer resulting in an edge shared double octahedral structure. This is the first pentahalide of the 5th main group with dimer structure.

The question whether AsCl_5 forms an intermediate between ionic structure and dimer structure could be answered. It was possible to grow single crystals and to analyze it by x-ray crystallography by low temperatures, even though AsCl_5 decomposes in AsCl_3 and Cl_2 above -30°C . AsCl_5 has a trigonal bipyramidal structure with two longer axial bonds and three shorter equatorial bonds. It is interesting to compare the different packing in AsCl_5 and SbCl_5 . If the whole molecules are considered to be simple spheres, then SbCl_5 has a regular hexagonal closest packing, AsCl_5 is packed body centered cubic.

In presence of water two salts could be isolated from the AsCl_5 solution containing the octahedral anion AsCl_6^- . The first compound contains AsOCl_3 molecules with an As-O double bond which is solvated with $\text{H}_5\text{O}_2^+\text{AsCl}_6^-$. The other compound forms H_5O_2^+ ions which are connected with Cl^- over hydrogen bonds.

BiCl_5 could not be isolated. It remains still a challenge for the future.

The known SbCl_4F is crystallized on another reaction way than the one known before. This comes as a surprise, since it results from a fluorine-chlorine-exchange with CFCl_3 .

POCl_3 and SbOCl_3 are well known compounds. By Raman spectroscopy for AsOCl_3 a monomeric structure was expected. This could not be confirmed. The crystal structure of AsOCl_3 reveals that it consists of a double oxygen bridged dimer with a trigonal bipyramidal structure environment around the arsenic atoms.

No answer could be found to the question of existence of the NOCl_2^+ cation.

Instead it was possible to grow single crystals of $[\text{ClSONC}_2\text{NCl}_2]^+\text{SbCl}_6^-$ from the same reaction that previously has been reported to form NOCl_2^+ . The novel cation consists of a $\text{C}_2\text{N}_2\text{SO}$ six membered ring.