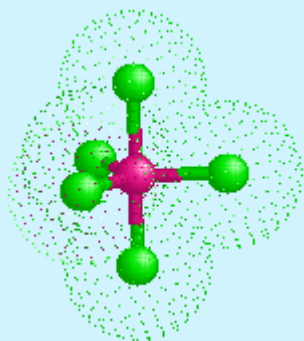


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# Arsenic Pentachloride - $\text{AsCl}_5$



(and some other  $\text{AX}_5$  molecules)

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Molecule of the Month January 2003  
Also available: [JSMol](#) version.

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## What's special about $\text{AsCl}_5$ ?

They said it couldn't be made.

## Why not?

$\text{PCl}_5$  and  $\text{SbCl}_5$  were first prepared in the early 19th century, but  $\text{AsCl}_5$  could not be made, and it was speculated that it was too unstable to exist.

## Was it?

Of course not, otherwise we wouldn't be reading this, but it took a special method to make it.

## How?

In 1976, the German chemist [Konrad Seppelt](#) (right) found that it could be prepared if a cold mixture of  $\text{AsCl}_3$  and  $\text{Cl}_2$  was irradiated with UV light at  $-100^\circ\text{C}$ ,



It decomposes at temperatures above  $-60^\circ\text{C}$ .



# Why does this method work?

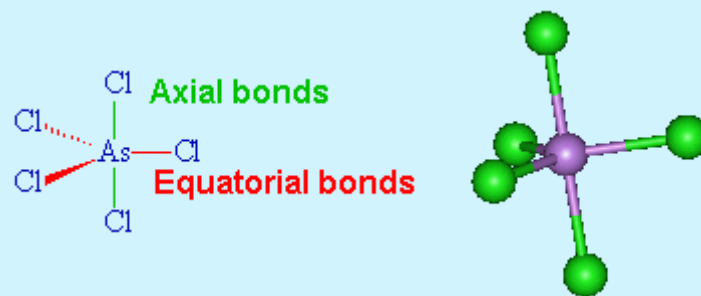
The UV light splits the chlorine molecule into reactive chlorine atoms, which can combine with the  $\text{AsCl}_3$  to form molecules of  $\text{AsCl}_5$  which have not got enough energy to shake themselves apart again.

## So how do we know $\text{AsCl}_5$ has been made, if it is only stable at low temperatures?

In his original study, Seppelt examined the vibrational (Raman) spectrum of the reaction mixture at regular intervals. As time went on, the spectrum changed from that of  $\text{AsCl}_3$  to one characteristic of  $\text{AsCl}_5$ , resembling the known spectra of  $\text{PCl}_5$  and  $\text{SbCl}_5$ . However, the clincher is that the structure of  $\text{AsCl}_5$  is now known.

## How did they do that?

A quarter of a century after his original discovery, Seppelt and his student Silvia Haupt succeeded in making yellow crystals of this unstable substance at  $-125^\circ\text{C}$  by crystallisation from solutions in  $\text{CH}_2\text{Cl}_2$ . X-ray diffraction studies show it has the expected trigonal bipyramidal structure in the solid state. The axial As-Cl distances are 220.7 pm whilst the equatorial As-Cl bonds are 210.6 and 211.9 (averaging 211.45) pm.

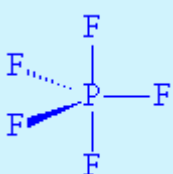
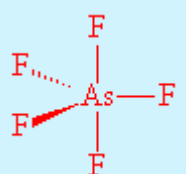


## Surely all the As-Cl bonds are the same?

No, they aren't. The electron pairs in the "axial" bonds have three  $90^\circ$  repulsions with electron pairs in the "equatorial" bonds, whilst the electron pairs in the equatorial bonds have only two  $90^\circ$  repulsions. It would therefore be predicted that repulsions involving the axial bonds would be stronger and that these bonds would therefore be longer, as is the case.

## Is that a one-off idea, or is it generally true?

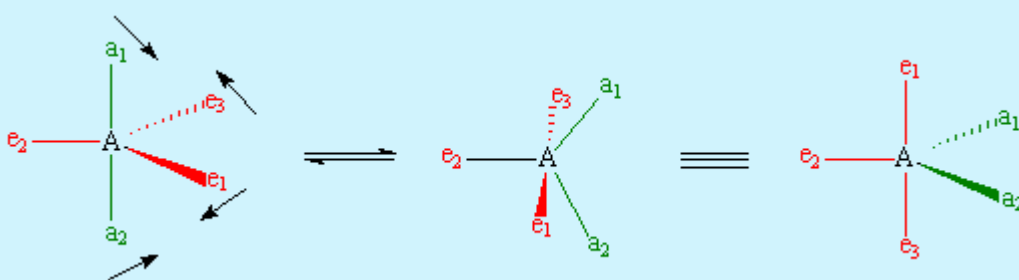
$\text{AsF}_5$  also has a trigonal bipyramidal structure, with As-F (axial) 171.9 pm and As-F (equatorial) 166.8 pm in the gas phase. Molecules of  $\text{AsF}_5$  are also present in crystals, having As-F (axial) 171.1 pm and As-F (equatorial) 165.6 pm.



$\text{PF}_5$  has a similar structure. Gas phase  $\text{PF}_5$  molecules have a  $D_{3h}$  structure (P-F (axial) 158 pm and P-F (equatorial) 153 pm ; in the solid state at  $-164^\circ\text{C}$ , P-F (axial) is 158.0 pm and P-F (equatorial) is 152.2 pm.

However, when chemists studied the  $^{19}\text{F}$  NMR spectrum of  $\text{PF}_5$ , they saw only one signal, even at  $-100^\circ\text{C}$ , showing there was only one environment for fluorines, which is not what was predicted. It has been suggested that there is interchange of fluorine atoms between

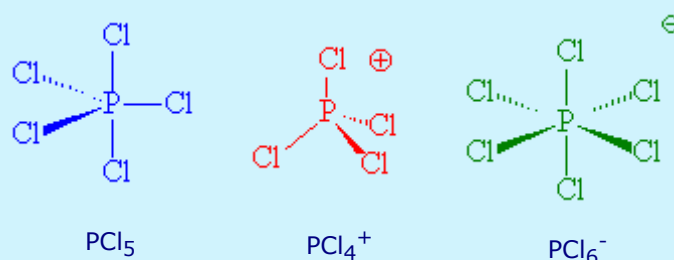
the axial and equatorial positions that is rapid on the NMR timescale, the so-called Berry pseudorotation (see image below), which proceeds via a square pyramidal intermediate. In this process, two equatorial bonds (shown in red) move away from each other and become axial bonds at the same time as the axial bonds (green) move together to become equatorial. Animations of this process can be seen in [Chime](#) or in [Quicktime](#).



The structure of  $\text{PCl}_5$  is even more complicated, however.

## How so?

In the gas phase, it does indeed contain  $\text{PCl}_5$  molecules, with P-Cl (axial) = 212.4 pm and P-Cl (equatorial) = 201.7 pm. However, crystals of  $\text{PCl}_5$  are composed of  $[\text{PCl}_4]^+$  and  $[\text{PCl}_6]^-$  ions. (P-Cl in the tetrahedral  $[\text{PCl}_4]^+$  ions is 190 pm whilst P-Cl in the octahedral  $[\text{PCl}_6]^-$  ions is 211-216 pm).



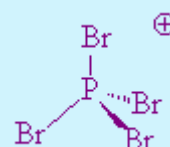
In addition to that, a metastable solid-state phase is also known that has the structure  $[\text{PCl}_4^+]_2 [\text{PCl}_6^-] \text{Cl}^-$ .

## And in solutions?

In polar solvents such as MeCN,  $\text{MeNO}_2$  or  $\text{CCl}_4$ , it is made of monomeric  $\text{PCl}_5$  molecules in association with a dimer.

## So $\text{PBr}_5$ does something similar?

No,  $\text{PBr}_5$  tends to change to a mixture of  $\text{PBr}_3$  and  $\text{Br}_2$  in the gas phase, whilst in the solid state,  $\text{PBr}_5$  is made of  $\text{PBr}_4^+$  and  $\text{Br}^-$  ions. The P-Br bond lengths in the  $\text{PBr}_4^+$  ions are 213 to 217 pm.



## Why is it different to $\text{PCl}_5$ ?

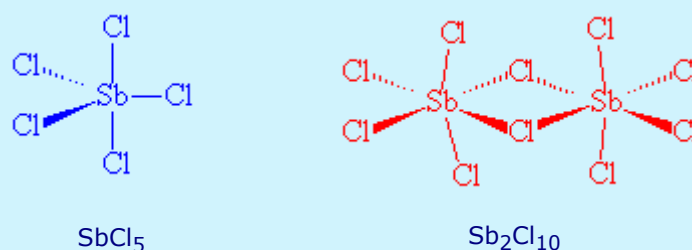
Because they are bigger than chlorine atoms, it seems that six bromines cannot attach to the same phosphorus atom, there are too many non-bonding repulsions.

## How about $\text{PI}_5$ ?

No one is sure if it exists. In 1978, it was reported to have been made, as black-brown crystals, from the reaction of  $\text{PCl}_5$  (in solution in  $\text{CH}_3\text{I}$ ) and  $\text{MI}$  ( $\text{M} = \text{Li}, \text{Na}$  or  $\text{K}$ ). However, so far there are no confirmatory reports of its structure.

## And $\text{SbCl}_5$ is complicated too?

No, it's relatively simple.  $\text{SbCl}_5$ , which is stable to  $140^\circ\text{C}$ , can readily be made from the reaction of  $\text{SbCl}_3$  and  $\text{Cl}_2$ . However, whilst solid  $\text{SbCl}_5$  has the expected molecular structure at room temperature, below  $-54.1^\circ\text{C}$  it changes reversibly to a dimeric molecule,  $\text{Cl}_4\text{Sb}(\mu\text{-Cl})_2\text{SbCl}_4$ . In the  $\text{SbCl}_5$  molecules,  $\text{Sb-Cl}$  (axial) distances are 233.3 pm and  $\text{Sb-Cl}$  (equatorial) distances are 227.04 pm.



## Why should this happen?

$\text{Sb}$  is a bigger atom than  $\text{As}$ , so it is not surprising that it finds it easier to accommodate six chlorine atoms round it. It is possible that  $\text{AsCl}_5$  could dimerise at very low temperatures, since six coordinate  $[\text{AsCl}_6]^-$  and  $[\text{AsCl}_5(\text{Me}_3\text{PO})]$  species are known.

## Why is $\text{AsCl}_5$ so unstable anyway?

The effect has been ascribed to the stabilisation of a  $4s^2$  electron pair in the elements following the 3d transition metals, caused by incomplete shielding of the nucleus lowering the energy of the 4s orbital and making it harder to promote 4s electrons. So  $\text{AsCl}_3$  is more stable than  $\text{AsCl}_5$ . A similar reason has been given for other facets of the behaviour of these elements, such as the difficulty in making the perbromate ion.

The capacity of chemistry to surprise is not exhausted, whilst the skill and ingenuity of modern chemists in studying molecules under unfavourable conditions continues to know no bounds.

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