# De structuur van I2Cl6(ICl3)

Boswijk, Klaas Harm

## SUMMARY

In the introduction some chemical and physico-chemical properties of the interhalogen compounds are reviewed. Making use of existing thermodynamical data their stability is discussed in some more detail.

The interhalogens, especially the higher ones, stimulated theoretical speculations about their structures. For the greater part the recent structure investigations on these compounds, however, are not in agreement with the theoretically proposed structures.

A contribution to the structure chemistry of the interhalogen compounds has been given by the determination of the crystal structure of $ICl_3$ by means of X-ray methods.

Ordinary and integrated Weissenberg photographs from the first nine levels about the needle axis of the crystals, as well as Laue-, oscillation- and flat film photographs were made. The interpretation of the photographs caused some difficulties, which could be overcome by assuming the crystals to consist of four complexly twinned triclinic individuals. The lattice constants are:

| | |
|---|---|
| $a = 5.71 \pm 0.03$ A$^o$ | $\alpha = 130^o50' \pm 10'$ |
| $b = 10.88 \pm 0.02$ A$^o$ | $\beta = 80^o50' \pm 20'$ |
| $c = 5.48 \pm 0.03$ A$^o$ | $\gamma = 10^o30' \pm 10'$ |

Two $ICl_3$ per unit cell; space groep $P\bar{1}$.

Because of the complexity of the reciprocal lattice only one – the [010] – projection was accessible for two dimensional Patterson and Fourier methods. The [010] Patterson synthesis was first tentativity interpreted in terms of flat $ICl_3$ molecules with valence angles of $120^o$. Fourier syntheses based on this structure could not be refined. A correct approximation to the structure was obtained by the application of the vector convergence method on the $(10\bar{1})$ Patterson section. It could be confirmed by a Fourier syntheses of the $(10\bar{1})$ section which, however, still showed considerable false detail. The atomic coordinates were refined by a sequence of ordinary and difference Fourier syntheses. The false detail proved to be partly due to incorrect scaling factors relating reflections of different layer lines, and partly to the finite series effect.

The latter could be reduced by the introduction of an artificial temperature factor. The final coordinates, corrected for the



remaining effect
of the back shift

The final value of

The crystal st
arranged in layers
the crystal may be

The molecules
point group symmet
ed by two chlorine
two others at 2.68

The molecular s
between valence pa
The possibility o
$ICl_2^+$- and $ICl_4^-$ ions

remaining effect of termination of the series by the application of the back shift method, are:

| | x | y | z |
|---|---|---|---|
| I | 0.0 | 67.0 | 0.0 |
| $Cl_1$ | 99.1 | 48.6 | 94.7 |
| $Cl_2$ | 97.9 | 167.2 | 92.7 |
| $Cl_3$ | 97.8 | 286.5 | 92.0 |

The final value of the disagreement index R is 0.12.

The crystal structure consists of molecules $I_2Cl_6$ which are arranged in layers $(10\bar{1})$. The two types of twinning occurring in the crystal may be explained by this structure.

The molecules are planar with negligible deviations from the point group symmetry mmm (fig. 15). Each iodine atom is surrounded by two chlorine atoms at a distance of 2.38 and 2.39 $A^O$ and by two others at 2.68 and 2.72 $A^O$.

The molecular structure is described in terms of a mesomerism between valence patterns involving $ICl_2^+$- and $ICl_4^-$ ions (pag. 67). The possibility of an average structure consisting of actual $ICl_2^+$- and $ICl_4^-$ ions could be excluded.