Structure of an Addition Compound Containing two Molecules of Iodine Monochloride and one Molecule of 1,4-Dioxan

O. HASSEL and J. HVOSLEF

Universitetets Kjemiske Institutt, Blindern-Oslo, Norway

It has been assumed that the interaction between an oxygen atom of an ether or a ketone with a halogen molecule results in a symmetrical bond type in which both halogen atoms take an equal part [1]. However, the first X-ray work on a solid addition product — the 1:1 compound between 1,4-dioxan and bromine [2] — revealed that in this case each ether oxygen is linked to *one* bromine atom only. Here the two atoms of a bromine molecule are situated

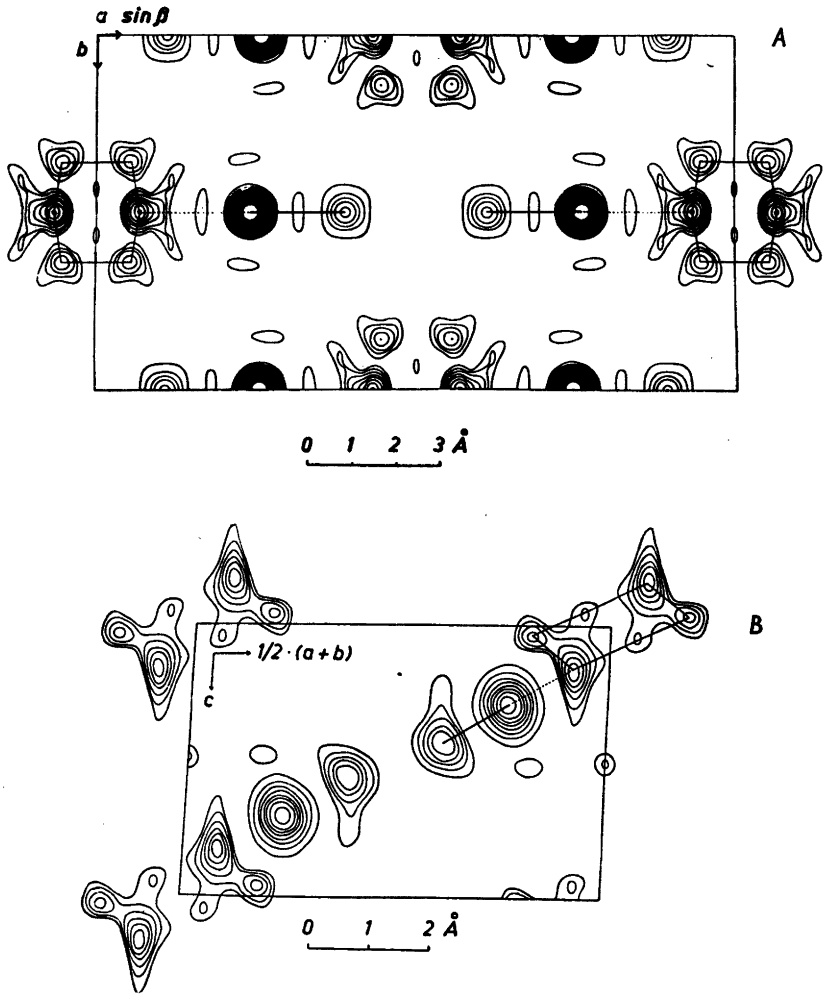

Fig. 1. Electron density maps projected. A) along [001]. Interval between contour lines for I and Cl:100 and between C and O:20. B) along [110]. Corresponding intervals are: I:100, Cl:30, C and O:10.

on the line joining the oxygen atoms of two neighbouring ether molecules. A similar structure is not to be expected if bromine is replaced by iodine monochloride, but we would expect the iodine atom to be directly linked to an ether oxygen and the angle O—I—Cl to be 180°. So far, we have not investigated this compound, but determined the structure of another compound which we obtained in the form of yellow needles (m. p. 103° C) directly from the vapours of the two compounds. Here the ratio of iodine monochloride and dioxan molecules is 2:1 as could easily be shown by dissolving the solid substance in an aqueous solution of potassium iodide and titrating the amount of iodine thereby set free.

The crystals of the new compound are *monoclinic* with $\beta = 95.2°$ and the space group is $C2/m$. The unit cell containing *four* molecules of iodine monochloride and two molecules of 1,4-dioxan have the constants $a = 14.62$, $b = 8.00$, $c = 4.56$. Approximate coordinates of the heavy iodine atoms could easily be found by conventional trial and error methods and Fourier maps computed using the signs of structure factors resulting from these coordinates. Only one refinement was necessary in order to arrive at the final maps reproduced in Fig. 1. The I and Cl coordinates thus obtained are: I: 0.242; 0; −0.290; Cl: 0.389; 0; −0.424. The coordinates of the light atoms derived from the maps are of course less accurate, but it is obvious that the centrosymmetrical dioxan molecules are of the "chair" form and the location of the oxygen atoms are good enough to show that each of them is linked to an iodine atom which has on its opposite side a chlorine atom, the O—I—Cl arrangement being linear or at least very nearly so. The O—I distance may safely be given as 2.6 Å, the I—Cl distance is 2.3 Å. The nearest Cl—Cl-approach, on the other side, is 3.38 Å showing that van der Waals forces only exist between chlorine atoms. The structure of the new compound thus provides a second example of a solid ether-halogen compound displaying a linear arrangement of the type O—Hal—Hal.

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2. Hassel, O. and Hvoslef, J. *Acta Chem. Scand.* **8** (1954) 873.

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Structure of an Addition Compound Containing *two* Bromine Molecules and one Molecule of Hexamethylene Tetramine

GUNNAR EIA and O. HASSEL

Universitetets Kjemiske Institutt, Blindern-Oslo, Norway

As part of a research programme dealing with crystal structures of addition compounds between ethers, amines *etc.* and inorganic molecules, a bromine compound which, according to analyses, contains two molecules of bromine on every molecule of hexamethylene tetramine has been investigated. The result of the X-ray work shows that each bromine molecule is linked to one of the four tertiary nitrogen atoms, the arrangement of both groups being the same. The N-Br-Br group is *linear* and the line through the three atoms in question is symmetrically situated with respect to the three C—N bonds of the nitrogen atom. Four tetrahedral bonds are thus found by each nitrogen atom involved. The bond angles do not deviate much from the "regular" angle (109.5°). The fact that the N-Br-Br angle is 180° (or at least very nearly so) rules out the possibility that resonance effects in the NBr_2 group based on equivalence of the two bromine atoms are of any significance. The two N-Br-Br groups of a molecular complex are crystallographically independent and the fact that they are found (within the limits of error) to be identical in shape is of considerable interest. The Br-Br distance is found equal to 2.4 Å; for the N-Br distance the value 2.3 Å was obtained. These findings point to a strong interaction between the nitrogen atom and the nearest bromine atom and indicate a very marked weakening of the Br-Br bond. It would appear rather probable that in addition compounds of amines showing markedly stronger basic properties than hexamethylene tetramine, a dissociation of the bromine molecule may even occur. Investigations dealing with addition compounds of such amines are now in progress in our laboratory.

The yellow crystals of the compound between hexamethylene tetramine and two molecules of bromine are *monoclinic* and belong to the space group $P2_1/c$.