Structure of Compounds between 1,4-Dioxan and Inorganic Substances

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The crystal structure of the compound formed by 1,4-dioxan and bromine has recently been determined [1]. The O—Br bond distance is very short — 2.71 Å — and the bond *direction* nearly corresponds to an "*e*" bond in *cyclo*hexane. At the same time the Br—Br bond distance nearly coincides with the distance in a free bromine molecule.

A structure investigation of the corresponding compound containing equal numbers of dioxan and mercuric chloride molecules has later been carried out. The structure is *triclinic*, not monoclinic, with a unit cell (space group $P\bar{1}$):

$a = 7.37$ $b = 7.12$ $c = 4.05$ $\alpha = 91.7°$
$\beta = 98.7°$ $\gamma = 67.9°$

containing *one* molecule of each species but geometrically related to the monoclinic C-centered cell of the bromine compound. The mercury atoms are in unique positions and determine the signs of the structure factors. A direct computation of electron density maps is therefore possible. In Fig. 1 a projection along the short (*c*) axis is reproduced. Besides the tilting of the dioxan rings (*cf.* the corresponding map for the bromine compound) the two structures differ also with respect to the position of the centers of the inorganic molecules along the *c*-axis: In the bromine compound the centers of bromine molecules are situated in planes midway between planes containing the centers of dioxan rings, whereas in the mercuric chloride compound mercury atoms and dioxan centers are all in the same levels. The planar arrangement of the two oxygen atoms and the two chlorine atoms surrounding a mercury atom thus corresponds to the arrangement of oxygen and chlorine atoms around the copper atom in addition compounds containing cupric chloride. The Hg—O distance is 2.66 Å, the Hg—Cl distance 2.34 Å.

It appears tempting to investigate structures of compounds containing more easily ionized halides. Some progress has already been made in the structure determination of compounds of dioxan with oxy-acids in which hydrogen bonding will be expected to play a decisive part. Furthermore, we have prepared a compound containing the substance of m. p. 135° C, believed to be a "naphtodioxan" [2], and mercuric chloride. A crystal structure investigation of this compound has been started in order to check the correctness of the assumed structure formula.

1. Hassel, O. and Hvoslef, J. *Acta Chem. Scand.* **8** (1954) 873.
2. Furberg, S. and Hassel, O. *Acta Chem. Scand.* **4** (1950) 1584.

Received November 11, 1954.

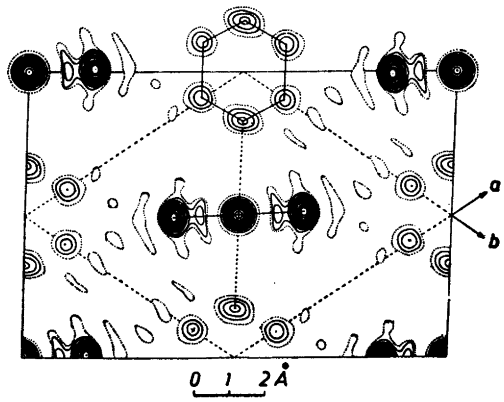

Fig. 1. Electron density map projected along the c*-axis. The* a*- and* b*-axes of the primitive unit cell are indicated by broken lines.*