

Crystal Chemistry of Binary Systems of Donor and Acceptor Molecules

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Unfortunately, thermodynamic measurements of charge-transfer equilibria in vapours are usually difficult and often virtually impossible. Most investigations have therefore been carried out in solution where the action of the third component — the solvent — is very difficult to assess. More weight should therefore, we think, be placed on condensed systems containing only donor and acceptor molecules. Structure determinations are also more promising in such systems.

In stoichiometric, crystalline compounds the mutual arrangement of the molecules of the more bulky partner might be expected to be at least nearly the same in crystals of this component and in its addition compound, at least when the van der Waals interaction energy in question makes a significant contribution to the total lattice energy. Such a situation is encountered in the 1:1 compounds formed by tetrabromoethylene,¹ resp. tetraiodoethylene² and pyrazine in which the packing of the larger acceptor molecules is nearly identical in crystals of the acceptor and in those of the addition compounds. In contrast to the acceptor crystals the adduct crystals are not isomorphous, although they both contain endless chains of alternating donor and acceptor molecules based on bonds between nitrogen and halogen atoms of nearly the same length (2.98 Å in the case of iodine, 3.02 Å in the case of bromine).

An interesting crystalline phase was found in the system hexamethylenetetramine-carbon tetrabromide in which an unbroken series of mixed crystals was observed with a mole percent of the acceptor ranging from zero to about sixty. Single crystal X-ray work was carried out

and showed that the cubic crystals are statistically disordered. The overstructure changes with the composition, but in all cases the subcell corresponds to the body-centered unit cell of the donor molecule, only slightly diminishing when the acceptor concentration increases. Fourier maps show that the bromine positions are close to those expected for a hypothetical body-centered modification of CBr_4 with these atoms situated exactly on the trigonal axes of the unit cell.

These mixed crystals between donor and acceptor molecules appear to be the first to be examined by X-rays, although indications have previously been observed of mixed crystal formation in donor-acceptor systems — from melting point diagrams³ and quite recently⁴ from IR spectra. It cannot be doubted that the formation of these phases depends on charge-transfer interaction between molecules which are so different in shape and size. As a further example we may mention the cryoscopic behaviour of dilute solution of iodine in benzene which, on cooling, deposits solid benzene containing iodine.

Iodoform and hexamethylenetetramine form a 1:1 compound of orthorhombic symmetry. The purest commercially available bromoform contains, however, so much carbon tetrabromide that even a redistilled sample proved to contain about 0.8 % per volume. For this reason our attempts to produce crystals of a compound with hexamethylenetetramine have failed so far. We only obtained the mixed crystals described above. It is possible that hexamethylenetetramine may be used to remove carbon tetrabromide from commercial bromoform.

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Received December 22, 1967.