

Crystal Structure of the Compound $C_6H_5N_2Cu_2Br_3$, an Intermediate in the Sandmeyer Reaction

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WHEN a Sandmeyer reaction is carried out at low temperature and in concentrated solution it is possible to isolate a crystalline, coloured complex of a diazonium salt and cuprous halide.¹ This compound has been supposed to be an intermediate in the Sandmeyer reaction and a structure determination might therefore shed light on the mechanism of this important reaction. We have therefore investigated the orange-red $C_6H_5N_2Cu_2Br_3$.

Crystal data: Orthorhombic, $a = 17.69$, $b = 5.72$, $c = 11.01$ Å, $Z = 4$. Systematic extinctions indicate space group $Pnma$ or $Pn2_1a$, the first of which was confirmed by the structure analysis. The structure was solved by using two-dimensional methods on the basis of 245 intensities from the $h0l$ zone and 70 from the $hk0$ zone. The intensities were measured photometrically on integrated Weissenberg films taken at $-25^\circ C$.

The structure determination was carried out using Patterson syntheses followed by Fourier refinements and finally by least-squares computations. The final R values were 9% for the $(h0l)$ and 11% for the $(hk0)$ data.

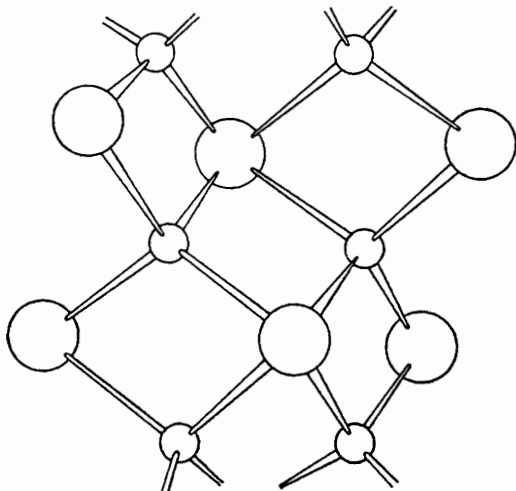
The lattice is built of normal benzenediazonium ions² and of $(Cu_2Br_3^-)$ ions. The benzenediazonium ions are situated in mirror planes parallel to (010) and they are well resolved in Fourier projections along the b -axis. Each of the "inner" nitrogen atoms is surrounded by four bromine atoms situated in a plane approximately perpendicular to the C-N-N direction with an N-Br distance of 3.65 Å. These bromine atoms belong to two anionic chains, both running parallel to the b -axis.

Along these chains two copper atoms alternate with three bromine atoms as shown in the Figure.

¹ A. Hantzsch, *Ber.*, 1895, **28**, 1752.

² Chr. Rømming, *Acta Chem. Scand.*, 1963, **17**, 1444.

The two copper atoms are related by a centre of symmetry, their interatomic separation is 3.09 Å whereas the Cu–Cu distance along the chain is only 2.86 Å.



The bromine atoms are situated in mirror planes perpendicular to the *b*-axis, and the arrangement around a copper atom is that of a distorted tetrahedron. One of the three bromine atoms of one link in the anionic chain is bonded to four copper atoms, the separation being 2.57 Å, the two other bromine atoms each form a bridge between two copper atoms with a Br–Cu distance of 2.45 Å. The bridging bromine atoms are expected to carry a negative charge since they are in direct contact with the N_2^+ group of the benzenediazonium ion.

Since most of the atoms of this structure occupy special positions, giving a well-resolved projection along the *b*-axis a marked increase in accuracy of atomic co-ordinates could not be expected from a full three-dimensional *X*-ray analysis, and further data were not collected.

Several suggestions have been made earlier as to the structure of this compound, some of them involving a bonding between atoms of the diazonium ion and the cuprous halide ion. No such contacts have been observed, however, and the intermediate in the Sandmeyer reaction must be regarded as a normal diazonium salt.

(Received, June 9th, 1965.)