The Crystal Structure of Di-(4-vinylpyridine)copper Dichloride. The Polymerization of the Vinyl Group

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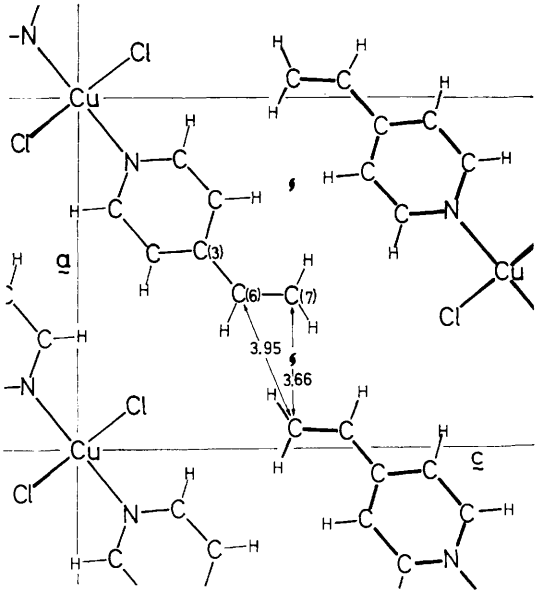
A LARGE series of 4-vinylpyridine (4-vpy) complexes of the 3*d* transition-metal chlorides have recently been prepared,[1] and subsequent work has shown that the identical stereoregular polymer of vinylpyridine can be obtained by simply heating single crystals of the cobalt, zinc, or copper complexes.[2] Crystal structure analyses have shown that the labile cobalt and zinc complexes have tetrahedral co-ordination.[3]

Turquoise laths of $Cu(4\text{-vpy})_2Cl_2$, recrystallized from *NN*-dimethylformamide, (supplied by Dr. N. Agnew), were monoclinic, space group $P2_1/n$, $a_0 = 8{\cdot}68$, $b_0 = 3{\cdot}91$, $c_0 = 21{\cdot}11$ Å, $\beta = 90{\cdot}0°$, $Z = 2$, $D_0 = 1{\cdot}60$, $D_c = 1{\cdot}60$. The molecule is required to be centrosymmetric with the copper atom at the origin. The chlorine-atom position was deduced from a three-dimensional Patterson summation; the positions of the nitrogen and carbon atoms were found from three-dimensional observed and difference Fourier maps, and the hydrogen atoms were clearly visible in the final difference map. The present R (excluding hydrogen atom contributions) is 0·15 for the 850 data observed with Cu-K_α radiation (R 0·19 for the 1350 recordable). Anisotropic least-squares refinement is beginning.

The co-ordination about the copper is square-planar with the expected bond lengths Cu–N = 2·01, Cu–Cl = 2·38 Å (e.s.d. about 0·02 Å). The atoms Cu, N, C(3), and C(6) lie within 0·02 Å of the *xz* plane, and the molecules are stacked parallel to the *b*-axis such that the Cl–Cu–Cl portions are twisted about the N–Cu–N axis giving a structure similar to that reported for $Cu(py)_2Cl_2$,[4] with Cl · · · Cu contacts of 3·02 Å.

Carbon atoms in adjacent vinyl groups are separated by only 3·91 Å parallel to the *b*-axis, and by 3·66 and 3·95 Å across the screw axis (Figure). These distances are considered to be very "short" for a compound that does not easily undergo polymerization. Hirshfeld[5] has suggested that 4·0 Å would be an upper limit for facile polymerization, yet in the tetrahedral cobalt and zinc derivatives, which polymerize far more easily, the closest contacts between adjacent vinyl groups ranged between 4·35 and 5·2 Å. The density of these tetrahedral compounds was only about 1·45 g./cc. and the thermal motion of the vinyl groups was very large,[3] the carbon atoms having B between 7 and 11 compared with 4 in the present case.

It thus appears that short intermolecular distances may be necessary, but certainly are not sufficient for ready polymerization. Far more important is the correct relative orientation of the reacting groups, which can occur when the molecules are loosely packed and the reacting groups undergo large thermal motion.



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