The Structure of Copper 8,12-Diethyl-2,3,7,13,17,18,21-heptamethylcorrole

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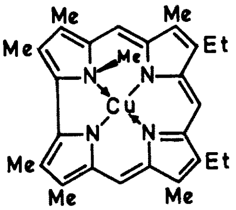
Summary The methylation of a copper corrole has been shown to take place on the nitrogen atom of ring A.

METAL corroles react with alkyl halides in the presence of bases to yield the alkylated derivatives, and in the case of some nickel corroles the n.m.r. spectra were interpreted as suggesting that the alkyl group was attached to the metal atom.[1] We now report the determination of the structure, by *X*-ray analysis, of the methylation product (MeI–NaOH–Me_2CO) of copper 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole which shows that substitution takes place on the nitrogen of ring A giving (I).†

The methyl compound crystallised as prisms from CH_2Cl_2–Et_2O. Oscillation and equi-inclination Weissenberg photographs (Cu-K_α radiation) showed that the cell is triclinic and contained two molecules. The assumption that the space group is $P\bar{1}$ was later justified by the success of the refinement. The unit cell parameters are:—$a = 16{\cdot}38 \pm 0{\cdot}04$, $b = 9{\cdot}76 \pm 0{\cdot}03$, $c = 8{\cdot}12 \pm 0{\cdot}03$ Å, $\alpha = 95°51'$, $\beta = 90°42' \pm 10'$, $\gamma = 96°54' \pm 10'$, $U = 1281$ Å^3, $D_m = 1{\cdot}271$, $Z = 2$, $D_c = 1{\cdot}254$.



(I)

Intensity measurements were made with a Hilger and Watts linear diffractometer using Mo-K_α radiation with the crystal rotating about its *c*-axis. Data were collected for the layers *hk*0—*hk*8 and 2777 reflections were sufficiently strong to be regarded as observed and were used in the structure determination. The copper atom was located by a three-dimensional Patterson synthesis and a subsequent three-dimensional Fourier synthesis phased on this atom revealed the whole structure of the molecule. Refinement was continued using the block-diagonal program developed by Dr. F. R. Ahmed of the N.R.C., Ottawa, and the final *R* value with all atoms treated anisotropically was 6·8%.

The bond lengths, bond angles, and planes of the molecule were then calculated and revealed the following facts. The *N*-alkylated ring has the β-β bond longer than the α–β bonds, whereas the other three five-membered rings have the opposite arrangement as is normal for porphins.[2] The N–methyl bond is slightly longer than usual at 1·54 Å (the Cu–Me distance is 2·7 Å). The alkylated ring is distorted markedly out of the plane of the rest of the molecule, the plane of the pyrrole making an angle of 23° with the mean plane defined by the *meso*-carbons, the α-pyrrole carbons and the three other nitrogen atoms. The alkylated ring itself does not appear to be planar but rather is folded across a line through the two α-carbon atoms, the angle of fold being about 10°.

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† G. C. Dobinson and R. Mason (Sheffield University) have also found that there is no evidence of a metal–carbon bond in the corresponding nickel corrole complex.

[1] R. Grigg, A. W. Johnson, and G. Shelton, *Chem. Comm.*, **1968**, 1151.

[2] E. R. Fleischer, C. K. Miller, and L. E. Webb, *J. Amer. Chem. Soc.*, **1964**, **86**, 2342.