X-Ray Crystal Structure of a 4:1 Amine Complex between Phthalocyanineiron(II) and 4-Methylpyridine

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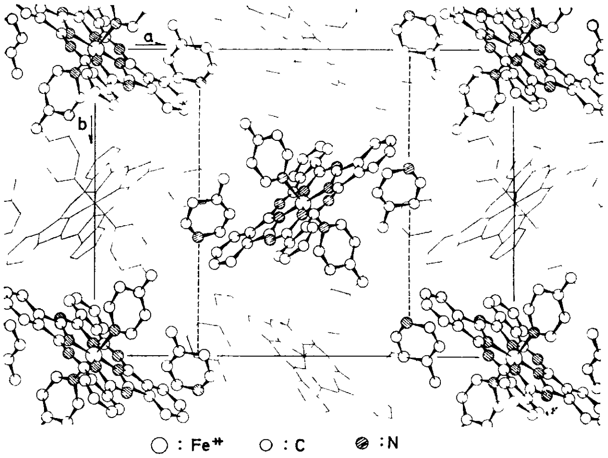
Summary A single-crystal *X*-ray diffraction study of the molecular complex between Fe^{II} phthalocyanine and 4-methylpyridine $[C_{32}N_8H_{16}Fe(C_6NH_7)_4]$ shows that two 4-methylpyridine molecules are co-ordinated at an octahedral Fe^{II} site with an N–Fe bond distance of 2·00 Å and that the other two are free molecules occluded in the structure

EXTENSIVE studies of phthalocyanine derivatives showed that metals such as zinc, cobalt, and iron, form crystalline stoicheiometric molecular complexes with various amines. Fe^{II} phthalocyanine was found to form complexes with molecular ratios 1 : 2, 1 : 4 and 1 : 6, according to the temperature and the kind of amine.

The 4-methylpyridine complex with the ratio 1:4 has been investigated by *X*-ray diffraction analysis to determine the bonding configuration of 4-methylpyridine to the phthalocyanine molecule. The crystal is orthorhombic, space group *Pbca*, $a = 25{\cdot}19$ (2), $b = 17{\cdot}86$ (2), $c = 10{\cdot}30$ (2) Å, D_m(flotation) $= 1{\cdot}339$, $D_c = 1{\cdot}336$ g cm^{-3} for $Z = 4$.

The crystal was sealed in a thin glass capillary with a drop of saturated 4-methylpyridine solution of Fe^{II} phthalocyanine. The intensity data were estimated visually from Weissenberg films taken with Fe-K_α radiation. The structure was determined by the heavy-atom method and has been refined by full-matrix least-squares methods employing anisotropic temperature factors for all non-hydrogen atoms, to an *R*-factor of 0·16.



FIGURE

The Figure shows a view of the structure seen down the *c*-axis. The Fe^{II} ion occupies a centre of symmetry, and is octahedrally co-ordinated by six nitrogens, four from the phthalocyanine ligand and two from 4-methylpyridine molecules. The phthalocyanine ligand is planar within $\pm 0{\cdot}07$ Å. The Fe–N (phthalocyanine) bond lengths are 1·92 Å on average indicating that the iron atom is in the low-spin state.

The two co-ordinated 4-methylpyridines are linked by Fe–N bonds of 2·00 Å, and their molecular planes are nearly parallel to the M-molecular axis and perpendicular to the phthalocyanine plane. The other two 4-methylpyridines have apparently no particular interactions with the complex as the intermolecular distances are too large. The crystal decomposition may be initiated by the loss of these unco-ordinated amine molecules when the crystal is left in air.

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