

A Novel Homoporphyrin System: Crystal Structure of the Nickel Complex

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Summary The nickel-complex of a new homoporphyrin was shown by X-ray analysis to be highly distorted compared to metalloporphyrins.

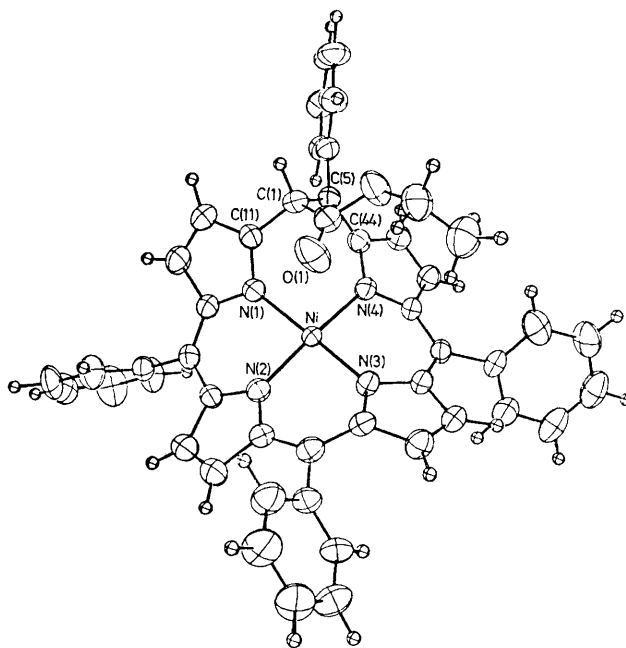
TREATMENT of the *N*-ethoxycarbonylmethyl *meso* tetraphenylporphin by Ni(acac)₂ led Callot and Tschamber¹ to a new and interesting homoporphyrin complex in the form of two stable epimers, *endo* and *exo* respectively. An azahomoporphyrin has previously been cited in the literature;² but unfortunately this was unstable. Thus, it is of great interest to specify the geometry of the present complex. Hence we examined the crystal structure of the *endo* species.

Suitable crystals were obtained by slow evaporation from a nitromethane-dichloromethane solution. Preliminary precession photographs showed only the required centre of symmetry and hence the space group is either *P*1 or \bar{P} 1, $a = 17.773(4)$, $b = 13.064(3)$, $c = 13.414(3)$ Å, $\alpha = 126.88(4)$, $\beta = 73.14(3)$, $\gamma = 125.68(2)^\circ$, $U = 2015$ Å³, $D_m = 1.25$, $D_c = 1.248$ g cm⁻³, $Z = 2$.

The intensities of 5516 non-zero independent reflections were recorded on a Picker four-circle diffractometer using Mo- K_α radiation. The choice of centrosymmetric space group *P*1 was confirmed by the structure determination. The structure was solved from the three-dimensional Patterson synthesis. Refinement describing the model with anisotropic thermal parameters for non-hydrogen atoms of the complex and of the CH₂Cl₂ solvate led to an actual discrepancy index *R* of 0.076.

The Figure shows a perspective view of the homoporphyrin complex with the essential atomic numbering scheme used. The co-ordination of the nickel atom can be considered as essentially square planar, involving the nitrogen atoms N(1), N(2), N(3) and N(4) of the four pyrrole bases. The Ni-N(4) bond length of 1.961(3) Å is longer than the other three which are equal to 1.885 ± 0.010 Å. This possibly results from the great distortion observed in the homoporphyrin ligand.

The pyrrole rings are planar but are rotated and inclined with respect to the four nitrogen least-squares (4N) plane. The angles between the (4N) plane and the planes of each of the N(1) to N(4) pyrrole nuclei are 43.6, 31.9, 24.0 and 33.4° respectively. Of particular interest is the large angle of 73.4° between the N(1) and N(4) pyrrole planes. Previously structural determinations have generally shown that much smaller departures from planarity are usually



observed for the porphyrinato core in porphyrins and metalloporphyrins.³ Thus the most striking deformation was found for a *N*-substituted porphyrin wherein the *N*-sub-

stituted pyrrole ring is tilted at 19.1° with respect to the plane of the other three nitrogen atoms.⁴

In the present structure, the observed distortion must be a result of the C(1) carbon insertion in the chain between N(1) and N(4) pyrrole rings of the original tetraphenylporphin. Indeed, the geometry around the C(1) carbon is consistent with sp^3 hybridization, but the C(11)–C(1)–C(5) bond angle is reduced to $99.9(4)^\circ$. This denotes a contraction partially compensated by an increase of the C(44)–N(4)–Ni bond angle to $130.5(3)^\circ$, and by the weakening of the Ni–N(4) bond length.

There is a dihedral angle of 80.6° between the (4N) plane and the plane defined by C(11), C(1), and C(5) carbon atoms. The ester group is bound to C(1) so that it lies above the (4N) plane towards the nickel atom. The O(1) ester oxygen is weakly, if at all, bonded to the metal, approaching the nickel at a distance of $2.938(6)$ Å.

Finally the phenyl groups are independently planar and are bound to the bridge positions between pyrroles through apparently shortened single bonds.

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