1:2 Metalloporphyrin–Nitroaromatic Sandwich Complexes: *X*-Ray Crystal Structure of One Such Complex

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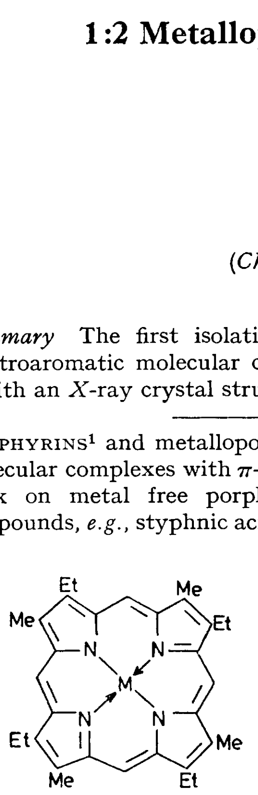
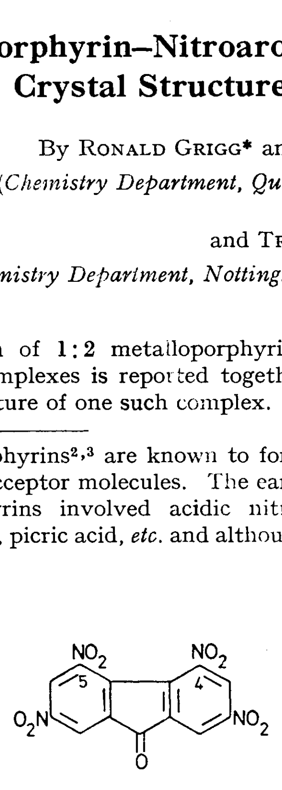
Summary The first isolation of 1:2 metalloporphyrin–nitroaromatic molecular complexes is reported together with an *X*-ray crystal structure of one such complex.

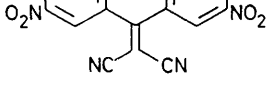
Porphyrins[1] and metalloporphyrins[2,3] are known to form molecular complexes with π-acceptor molecules. The early work on metal free porphyrins involved acidic nitro-compounds, *e.g.*, styphnic acid, picric acid, *etc.* and although both 1:1 and 1:2 complexes (porphyrin: nitro-compound) were formed it seems likely that these involve protonation of the porphyrin system (salt formation). Metalloporphyrin molecular complexes involving self-association[4] (*e.g.*, chlorophyll dimers in the reaction centre in photosynthesis) and π–π complex formation with, *e.g.*, quinones[5] and aromatic amino-acid side chains in haemoproteins,[6] are important in biological processes and this has prompted a number of *in vitro* studies. Most of the *in vitro* work on metalloprophyrin molecular complexes has involved spectroscopic studies on solutions containing varying amounts of π-acceptor (often nitroaromatic compounds) and the spectroscopic results have been analysed in terms of 1:1 complexes even though very high molar ratios of π-acceptor: metalloporphyrin were used. Recently Castro[7] reported the results of solution redox chemistry involving iron porphyrins and quinones, hydroquinones, and nitro-aromatics.



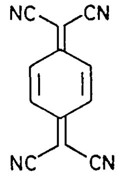
(1)



(2)



(3)



(4)

We now report the isolation of two metalloporphyrin–π-acceptor 1:2 molecular complexes. Thus evaporation of a solution of the nickel(II) etioporphyrin I (**1**; M = Ni^{II}) and the tetranitrofluorenone (**2**) in chloroform gave both the 1:1 and 1:2 complexes.† Similarly the cobalt porphyrin (**1**; M = Co^{II}) gave a 1:2 complex (56%) with (**3**); a 1:1 complex (46%) of (**1**; M = Ni^{II}) and (**4**) has also been isolated. The possibility of the presence of some 1:2 complex in solutions of metalloporphyrins and π^6-acceptors was suggested by earlier workers[8,9] but has been largely ignored in more recent work. In particular 1:2 cobalt(II) *meso*-tetra-*p*-tolylporphyrin: nitroaromatic complexes were detected in toluene glasses at low temperature.[9] The *X*-ray crystal structure of the 1:2 complex of (**1**; M = Ni^{II}) with (**2**) has been determined.

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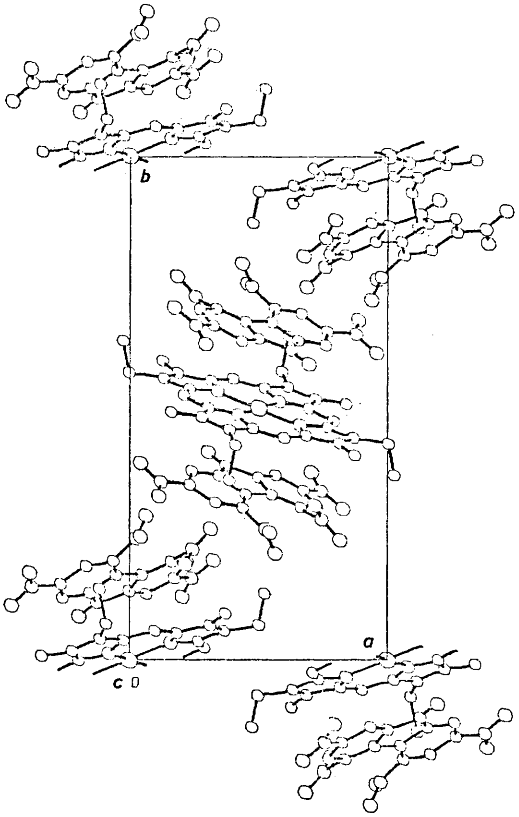
† The solution contained (**1**; M=Ni^{II}) and (**2**) in a 1:2 molar ratio and a mixture of both 1:1 and 1:2 complexes was obtained. The mixture was separated manually.

Crystal data: $\frac{1}{2}$ $(C_{32}H_{36}N_4Ni)\cdot C_{13}H_4N_4O_8$, M 611·9, monoclinic, a = 12·801(2), b = 20·838(3), c = 12·088(2) Å, β = 123·0(1)°, U = 2704·2 Å^3, D_c = 1·504, D_m = 1·495 g cm^{-3}, Z = 4, $F(000)$ = 1264; space group $P2_1/n$, from systematic absences, Mo-K_α radiation (graphite monochromator), λ = 0·71069 Å, μ = 4·5 cm^{-1}.

Intensities were measured out to $\theta \leqslant 25°$ (w = 2–2θ mode) and a total of 3257 reflections with a net count of $I \geqslant 3\sigma(I)$ were used in the refinement. The structure was solved using the centrosymmetric direct methods program of SHELX. As had already been deduced from the unit cell contents, the porphyrin fragment occupies a special position with the nickel atom at a centre of symmetry. Refinement by least-squares proceeded satisfactorily up to a point. A difference map plotted to locate hydrogen atoms showed these but also showed several peaks (stronger than those attributable to hydrogen) in chemically unacceptable positions in the neighbourhood of the nitro-groups at positions 4 and 5 of the fluorenone ring. These two nitro-groups had appeared distorted (non-planar, unequal N–O bond lengths) and we had assumed this distortion to be real and due to steric crowding. After structure factor calculations omitting the six atoms of the two nitro-groups, a difference map showed peaks corresponding to two planar nitro-groups with very nearly equal N–O bond lengths. However, refinement of these positions resulted in a movement of the atoms back to the distorted arrangement. Efforts are still in progress to resolve this anomaly. The current R-value with non-hydrogen atoms treated anisotropically and hydrogen atoms included in fixed positions with U = 0·05 and the porphyrin and fluorenone fragments being refined in separate blocks, is 7·8.‡



FIGURE

The above problem does not affect the general conclusions concerning the gross structure of the complex. The porphyrin and fluorenone rings are both approximately planar and the cell contains two pseudo molecules in special positions, each consisting of a porphyrin sandwiched strictly symmetrically between two tetranitrofluorenone molecules which must be parallel to each other because of symmetry. The angle between the porphyrin and fluorenone planes is 11·4° and the fluorenone ring is tilted with respect to the porphyrin so that the carbonyl oxygen is nearest the porphyrin mean plane (2·97 Å) and the two benzenoid carbon atoms *para* to the carbonyl group are 3·91 and 3·60 Å from that plane. The nickel atom is 3·33 Å from the mean plane of the fluorenone ring. A fully detailed analysis of the geometry of the complex must await clarification of the geometry of the nitro-groups. The diagram (Figure) of the cell looking along the c-axis shows the sandwich nature of the complex.

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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