Crystal Structure of the Nickel Complex of 2,3,7,8,12,13,17,18-Octaethyl-1,19(21*H*,24*H*)-bilindione (Octaethylbilatriene-*abc*)

By Joseph V. Bonfiglio, Raymond Bonnett, Michael B. Hursthouse, and K. M. Abdul Malik
(*Chemistry Department, Queen Mary College, Mile End Road, London* E1 4NS)

Summary The preparation and *X*-ray structure determination of a metal complex of a bile pigment model compound are reported; the nickel complex of octaethylbilatriene-*abc* takes up a helical conformation, with the four nitrogen ligands deviating significantly from a square-planar arrangement.

In recent years the chemistry of porphyrins and metalloporphyrins has been considerably illuminated by investigations on appropriate model compounds, particularly octaethylporphyrin. Interest in the linear tetrapyrrole series merits a similar reawakening, not least because of the biological importance of such compounds in haem catabolism, photosynthesis, and photoperiodism. As with the porphyrins the natural examples have a complex substitution pattern which hampers studies on the fundamental reactivity of the heterocyclic system. We consider octaethylbilatriene-*abc* [**1**, also called 2,3,7,8,12,13,17,18-octaethyl-

1,19(21*H*,24*H*)bilindione][1] to be a valuable model here, and report the preparation and *X*-ray structure analysis of the nickel complex (**2**) of this compound. This appears to be the first structural analysis of a metallobilin-1,19-dione: Fuhrhop and his colleagues[2] have recently reported structure analyses of zinc complexes of a related 19-formylbilin-1-one.

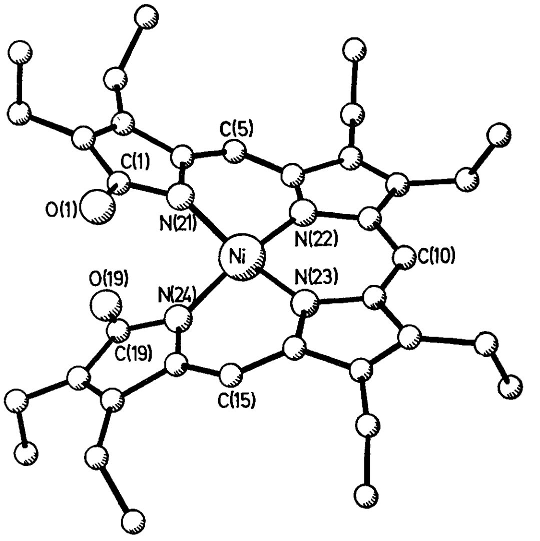
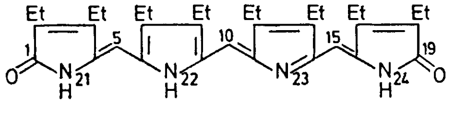


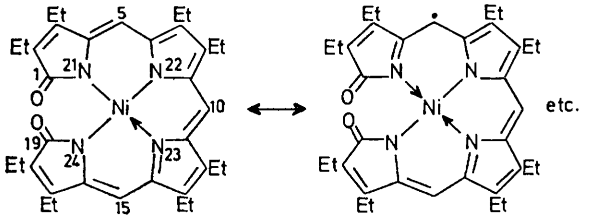
Figure. Nickel complex (**2**) of octaethylbilin-1,19,dione.

Treatment of (**1**) with nickel acetate tetrahydrate in ethanol gave dark green crystals of the nickel complex from chloroform–cyclohexane which analysed for $C_{35}H_{44}N_4NiO_2$ (or $C_{35}H_{43}N_4NiO_2$) *i.e.* a 1:1 complex without additional ligands. Spectroscopic data: *m/e* 610·284 ($C_{35}H_{44}N_4{}^{58}NiO_2$ requires 610·282); λ_{max} ($CHCl_3$) 300 (ϵ 21,000), 261 (25,600), 435 (22,100), 600 (4800; plateau 570—620 nm), and 773 (7700) nm. *Crystal data:* monoclinic, $a = 14{\cdot}812$, $b = 18{\cdot}743$, $c = 12{\cdot}956$ Å; $\beta = 118{\cdot}02°$; $U = 3175$ Å^3; F(000) = 1292; space group *C*2/*c*; Z = 4; $D_c = 1{\cdot}28$ g cm^{-3}; $D_m = 1{\cdot}29$ g cm^{-3}; μ(Mo-K_α) = 6·5 cm^{-1}. The intensities of 1486 independent reflections, in the range $1{\cdot}5 < \theta < 20°$, were measured on a Nonius CAD4 diffractometer using Mo-K_α radiation. Of these only 686 reflections obeyed the conditions $|F_0| > 3\sigma|F_0|$ and were used in the subsequent solution by Patterson and Fourier methods. Least-squares refinement has given $R = 0{\cdot}053$, and the resulting molecular structure is shown in the Figure.†

The molecule possesses a two-fold axis of symmetry through Ni and C(10). It has a helical shape, with the two ends of the helix in close proximity [O(1)–O(19) *ca.* 3 Å]. The average Ni–N distance (1·886 Å) is, as expected, slightly shorter than the corresponding values in nickel octaethylporphyrin in either its triclinic[3] (planar conformation, 1·96 Å) or tetragonal[4] (ruffled conformation, 1·93 Å) forms. To accommodate the repulsive interactions of the terminal oxygen atoms, the co-ordination geometry about nickel is a severely distorted square plane. Deviations of the nickel and four nitrogen atoms from their mean plane are Ni, 0; N(22), N(23), ±0·292; and N(21), N(24), ±0·296 Å. The individual pyrrole rings are essentially planar. Rings B and C are inclined at 17·2°, and rings A and D at 29·8°, to the mean plane of the four nitrogen atoms. Because of the space group symmetry the unit cell is required to contain equal numbers of the enantiomeric forms (*i.e.* right and left hand helices) of the compound. It seems likely that this type of compound could be resolved and, if so, the enantiomers would be expected to show marked chiroptical effects.



(1)



(2)

The paramagnetism[5] of this complex ($g_{\parallel}$ 1·980, $g_{\perp}$ 2·011 at 77 K) and the absence of gegenions lead us to regard it in terms of canonical forms such as Ni^{II} (free base − 3H$^+$ − e)$^{2-}$ ⟷ Ni^{III} (free base − 3H$^+$)$^{3-}$, a view which will be considered in detail in the full paper.

We are grateful to Dr. K. D. Sales for discussions of the e.s.r. results and to the M.R.C. for research support.

(*Received*, 8*th November* 1976; *Com.* 1234.)

---

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

[1] R. Bonnett and M. J. Dimsdale, *J. C. S. Perkin I*, 1972, 2540.
[2] G. Struckmeier, U. Thewalt, and J. H. Fuhrhop, *J. Amer. Chem. Soc.*, 1976, **98**, 278.
[3] D. L. Cullen and E. F. Meyer, *J. Amer. Chem. Soc.*, 1974, **96**, 2095.
[4] E. F. Meyer, *Acta Cryst.*, 1972, **B28**, 2162.
[5] J. Subramanian, J. M. Fuhrhop, A. Salek, and A. Gossauer, *J. Magnetic Resonance*, 1974, **15**, 19.