

## Alkyl- and Aryl-metal(III) Complexes of Aetioporphyrin I

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WE have described<sup>1</sup> the synthesis of methyl- and ethyl-cobalt(III) complexes of aetioporphyrin I by the reaction of the pyridinobromocobalt(III) porphyrin complex with the alkylmagnesium halide. The reaction has now been extended to include the *n*-propyl-, *n*-butyl-, phenyl- (from phenyl-lithium), *m*-tolyl-, and *p*-tolyl-cobalt(III) aetioporphyrin I complexes in order to assess the shielding effect of the porphin ring on the n.m.r. signals of the protons of the alkylcobalt (Table) and arylcobalt substituents. It is recognised that the cobalt atom also contributes to this shielding effect, for the methyl resonance in methylcobalt compounds lacking the porphin ring is at  $\tau$  9–10,<sup>2,3</sup> but this effect is much smaller than that of the porphin ring current.

the interaction. Unfortunately the solubility of the phenylcobalt(III) derivative precluded the measurement of its n.m.r. spectrum but the methyl signals of the *p*- and *m*-tolyl derivatives appeared at  $\tau$  8.9 and 9.3 respectively. The magnitude of the shielding effect of the porphin is emphasised by the fact that the methyl group of the *p*-tolyl derivative is approximately 6 Å above the plane of the porphin ring. The aromatic protons of the *p*-tolyl derivative formed an AB system with the high-field doublet centred at  $\tau$  10.3, but the other half of the AB system was obscured by the signals of porphin  $\beta$ -alkyl substituents.

We have also prepared crystalline octahedral ethyl- and *p*-tolyl-iron(III) complexes of aetioporphyrin I by a similar method. Analysis

TABLE. N.m.r. signals\* ( $\tau$ -values) of protons of cobalt-alkyl substituents of Aetioporphyrin I complexes in deuteriochloroform

Cobalt(III) substituent	$\alpha$ -Carbon atom	$\beta$ -Carbon atom	$\gamma$ -Carbon atom	$\delta$ -Carbon atom
Me	15.15 (s)	—	—	—
Et	14.4† (m)	15.67 (t)	—	—
Pr <sup>a</sup>	14.4 (m)	15.2 (m)	11.9 (t)	—
Bu <sup>a</sup>	14.3 (m)	15.3 (m)	11.65 (m)	11.0 (t)

\* The spectrum of the *n*-butylcobalt derivative was measured on a Jeol 100 Mc./sec. instrument using a CAT (Computer of Average Transients). We thank Dr. R. J. P. Williams and his associates, University of Oxford, for this determination. The remaining spectra were measured on a Perkin-Elmer 60 Mc./sec. instrument.

† This figure was quoted incorrectly in our earlier Communication.

The maximum effect of the aromatic porphin ring is thus exerted on the protons of the  $\beta$ -carbon atom, and a further increase in the distance from the ring causes a rapid decrease in the magnitude of

indicates that the sixth ligand is water in both cases. These iron(III) complexes are paramagnetic and do not show n.m.r. spectra. However, like the cobalt(III) analogues, they are sensitive to light,

especially in solution, and the stability of the solutions depends on the polarity of the solvent. The photolytic decomposition of solutions in acetone or ethanol is much more rapid than that of benzene or cyclohexane solutions.

The alkylcobalamins, in contrast, are normally prepared<sup>4</sup> by the action of alkyl halides on the reduced species, B<sub>128</sub>, which can be regarded<sup>4,5</sup> as a cobalt(I) hydride. Both preparative methods have been used for the formation of the alkylcobalt(III) derivatives of dimethylglyoxime.<sup>6</sup> Although earlier attempts to reduce octahedral cobalt(III) porphyrin complexes led to the production of planar cobalt(II) derivatives,<sup>7</sup> we have now found that reduction of cobalt(II) aetioporphylin I with 1% sodium amalgam in dry degassed pyridine or 1,2-dimethoxyethane, (*cf.* ref. 8) gave a cobalt(I) species which, unlike its cobalt(II) precursor, showed an

n.m.r. spectrum. This (pyridine solution) included signals at  $\tau$  0.56 (s; *meso*-protons), 6.66 (q;  $J = 7$  c./sec.; methylenes of ethyl groups), 7.3 (s; nuclear methyl groups) and 8.4 (t;  $J = 7$  c./sec.; methyls of ethyl groups). Treatment of this product with ethyl iodide gave the crystalline ethylcobalt(III) complex, spectroscopically identical with that produced from pyridinobromocobalt(III) aetioporphylin I and ethylmagnesium bromide. The scope of the method was extended by the demonstration that the crystalline acetylcobalt(III) aetioporphylin I complex was formed in good yield by reaction of acetic anhydride with the cobalt(I) species. The n.m.r. resonance associated with the acetyl methyl group in the acetylcobalt(III) derivative occurred at  $\tau$  12.97 and the i.r. spectrum (KBr disc) showed a strong band at 1722 cm.<sup>-1</sup>

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<sup>1</sup> D. Dolphin and A. W. Johnson, *Chem. Comm.*, 1965, 494.

<sup>2</sup> H. A. O. Hill, J. M. Pratt, and R. J. P. Williams, *J. Chem. Soc.*, 1965, 2859.

<sup>3</sup> H. Yamazaki and N. Hagihara, *Bull. Chem. Soc. Japan*, 1965, 38, 2212.

<sup>4</sup> A. W. Johnson, L. Mervyn, N. Shaw, and E. Lester Smith, *Nature*, 1962, 194, 1175; *J. Chem. Soc.*, 1963, 4146; K. Bernhauer, O. Müller, and G. Müller, *Biochem. Z.*, 1962, 336, 102, 299.

<sup>5</sup> G. N. Schrauzer, R. J. Windgassen, and J. Kohnle, *Chem. Ber.*, 1965, 98, 3324.

<sup>6</sup> G. N. Schrauzer and J. Kohnle, *Chem. Ber.*, 1964, 97, 3056.

<sup>7</sup> A. W. Johnson and I. T. Kay, *J. Chem. Soc.*, 1960, 2979.

<sup>8</sup> H. W. Whitlock and B. K. Bower, *Tetrahedron Letters*, 1965, 4827.