Nuclear Magnetic Resonance of Molecular Complexes of Cobalt(II) Mesoporphyrin IX Dimethyl Ester

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THE formation of complexes between metal porphyrins and aromatic nitro-compounds has been described[1,2] and their isolation reported[2]. We have investigated the effect of cobalt(II) mesoporphyrin IX dimethyl ester on the ^{1}H n.m.r. spectra of some aromatic nitro-compounds in deuterochloroform solution. The measurements were made at 100 Mc./sec. and 31° using a JEOL JNM-4H-100 n.m.r. spectrometer. The chemical shifts, relative to Me_4Si, were measured using a frequency counter. The porphyrin concentration was usually held constant at *ca.* 9×10^{-4}M and the concentration of the aromatic compound varied between 0·004 and 0·180 M.

At constant cobalt(II) mesoporphyrin IX dimethyl ester concentration, the reciprocal of the chemical shift of the hydrogens in the aromatic nitro-compounds, *e.g.*, 1,3,5-trinitrobenzene, was proportional to the aromatic compound concentration, moving to higher field with decreasing aromatic compound concentration (see Figure). Assuming a 1 : 1 complex,[2] the results can be analysed using the equation,

$$K\mathrm{P}(\Delta_0/\Delta) - K\mathrm{P} = 1 + K\mathrm{A}(1-\Delta/\Delta_0)$$

where $K = [\mathrm{PA}]/[\mathrm{P}][\mathrm{A}]$, [P] = concentration of free porphyrin, [A] = concentration of free aromatic compound, P = total concentration of

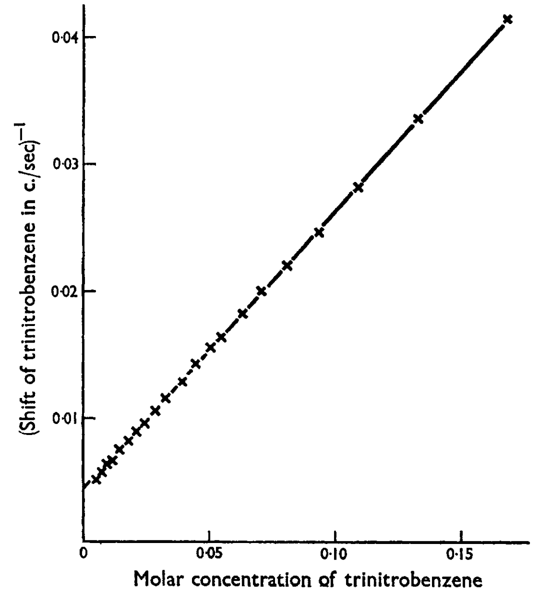

FIGURE.

Relationship between the chemical shift (Δ) *of the protons in* 1,3,5-*trinitrobenzene and the concentration* (A) *of* 1,3,5-*trinitrobenzene in the presence of cobalt*(II) *mesoporphyrin* IX *dimethyl ester* (9×10^{-4}M) *in* $CDCl_3$ *at* 31°.

porphyrin, A = total concentration of aromatic compound, [PA] = concentration of complex, Δ = observed shift of the resonance relative to that of the free aromatic compound and Δ_0 = the shift of the fully-formed complex relative to that in the free aromatic compound. As $1 - \Delta/\Delta_0$ was close to 1 in all our experiments, Δ_0 could be obtained from the gradient which is $1/P\Delta_0$. The intercept, $1/KP\Delta_0 + 1/\Delta_0$ enables an approximate stability constant to be calculated for the complex. The stability constants calculated in this way are in fair agreement with those derived from spectrophotometric measurements.[2] Correction for the $1 - \Delta/\Delta_0$ term does not produce a significant change in Δ_0 or K. A more detailed analysis of the results indicate that there may be formation of some 1:2 complex and calculations based on this are proceeding.

The observation of an only slightly broadened resonance for the aromatic hydrogens even when complexed with the paramagnetic cobalt(II) mesoporphyrin is due[3] to either the relaxation time of the unpaired electron in the d^7 ion or the half-life of the complex or both being considerably shorter than $1/\Delta_0$ sec. That due to the unpaired electron is probably short since the electron spin resonance spectrum of cobalt porphyrin cannot be observed[4] at temperatures much above 77° though at liquid-nitrogen temperature it gives a spectrum interpretable in terms of a low spin d^7 ion with $g_\perp = 2{\cdot}286$ and $g_\parallel = 2{\cdot}079$. The large shift observed for the complex is either a contact shift or a pseudo-contact shift, the latter being permissible because of the anisotropy of the g-value. The magnitude of a contact shift is simply related to the unpaired electron density on the carbon atom adjacent to the hydrogen which is shifted. However, the 2,6-hydrogens in 3,5-dinitrobenzonitrile are shifted in the same direction and by nearly the same amount as the non-equivalent 4-hydrogen. This disagrees with the predictions of a McLachlan treatment of 3,5-dinitrobenzonitrile and also with the e.s.r. of the radical anion,[5] assuming that the electron density would be transferred to the first unfilled molecular orbital. We conclude, therefore, that the dominant effect causing the shift is the pseudo-contact term where the shift is related to the relative position of the hydrogens in the aromatic compound and the unpaired electron on the cobalt. Preliminary calculations indicate that the aromatic compound is above one of the pyrrole rings.

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